According to the Punjab, Federal & Azad Kashmir Boards

Scholar Series

REVISED Edition

Chemistry

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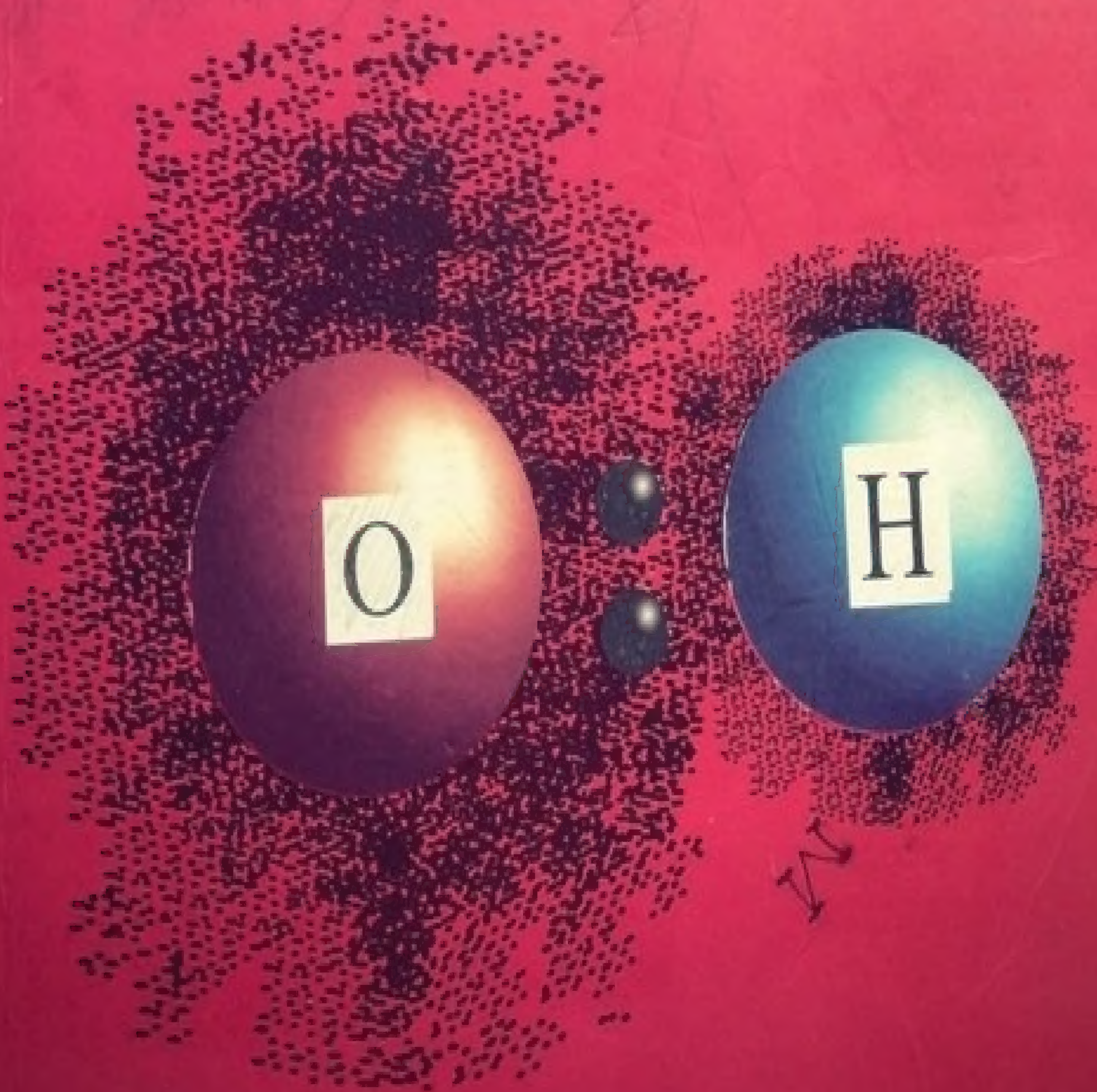
Subjective



Chapter 1

BASIC CONCEPTS

HISTORICAL BACKGROUND OF ATOM

Greek philosophers

Greek philosophers thought that matter could be divided into smaller and smaller particles to reach a basic unit which could not be further sub-divided. **Democritus** named these smallest indivisible particles as atoms derived from "atomos" which means indivisible. These ideas of Greek philosophers were not based on experimental evidences.

Dalton's atomic theory started chemistry on the road from a branch of philosophy to the science which it is today.

17th Century work

In the late 17th century, the quantitative study of the composition of pure substances disclosed that a few elements were the components of many difficult substances. It was also investigated that how elements combined to form compounds and how compounds could be broken down into their constituent elements.

Dalton's work

In 1808, an English school teacher, John Dalton recognized that law of conservation of mass and law of definite proportions could only be explained by the existence of atoms. He developed a theory about atom called **Dalton's Atomic Theory**. The main postulate of atomic theory is that all matter is composed of atoms of different elements, which differ in their properties.

Element

A substance consisting of atoms which all have the same number of protons i.e. the same atomic number. Elements are chemically the simplest substances and hence cannot be broken down further using chemical methods. Elements can only be changed into other elements using nuclear methods.

Atom

The smallest particle of an element which can take part in a chemical reaction is called **atom**.

or

The smallest particle of an element which may or may not exist independently is called **atom**.

Examples

Atoms of **He, Ne, Ar, Kr, Xe** and **Rn** can exist independently while atoms of **H, O, N** etc. do not exist independently.

Sub-atomic particles

According to modern researches, atom is composed of sub-atomic particles like electron, proton, neutron, hypron, boson, neutrino, antineutrino etc. More than 100 such particles are thought to exist in an atom. However, electron, proton and neutron are regarded as fundamental particles of atoms.

Berzelius's work

Swedish Chemist J. Berzelius (1779 – 1848) has following contribution in chemistry

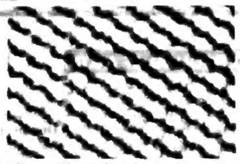
- He determined the atomic masses of elements. A number of his values are close to the modern values of atomic masses.
- He developed the system of giving element a symbol.

J.Berzelius (Best experimental chemist) performed more than 2000 experiments over a 10 years period to determine atomic masses for 50 elements then known.

Comparison of Berzelius's atomic masses with modern values

Element	Berzelius value	Current value
Chlorine	35.41	35.45
Copper	63.00	63.55
Nitrogen	14.05	14.01

Berzelius discovered cerium, thorium, selenium and silicon.



Electron microscopic photograph of graphite

Evidence of Atoms

It is not possible actually to see the atoms but the nearest possibility to its direct evidence is by using an electron microscope. A clear and accurate image of an object that is smaller than the wavelength of visible light, cannot be obtained.

Demerit of compound microscope

An ordinary optical microscope can measure the size of an object up to or above 500 nm (1 nm = 10^{-9} m).

Use of electron microscope

The objects of the size of an atom can be observed in an electron microscope. It uses beams of electrons instead of visible light, because wavelength of electron is much shorter than that of visible light and is most suitable for viewing the atoms.

Electron microscopic photograph of graphite

The figure shows electron microscopic photograph of a piece of graphite which has been magnified about 15 millions times. The bright band in the figure are layers of carbon atoms.

Results of X-rays work

In the twentieth century, X-rays work has shown that

- **Diameter of atoms** are of the order 2×10^{-10} m which is 0.2 nm or 2 $\mathring{A}$.
- **Masses of atoms** range from 10^{-27} to 10^{-25} kg. They are often expressed in atomic mass units (amu)

$$1\ \text{amu} = 1.661 \times 10^{-27}\ \text{kg}\ (1.661 \times 10^{-24}\ \text{g or}\ 1.661 \times 10^{-21}\ \text{mg})$$

Consequence

This shows that the atoms do exist and they are of an amazingly small size. Even a full stop may have two million atoms present in it.

Amazingly Small Atoms:

- If a golf ball is magnified to the size of the earth, then an atom would be the size of marble.
- Take a deep breath, you have just breathed 10^{5} million atoms.

$1\ \mathring{A} = 10^{-10}$ m

Molecule

"The smallest particle of a pure substance (element or compound) which can exist independently is called a molecule."

Classification of Molecules

On the basis of **(i) Nature** **(ii) Atomicity** **(iii) Size**

(i) On the basis of it nature

On the basis of nature, molecules are of two types.

(a) Homo-atomic molecules

(b) Hetero-atomic molecules

(a) Homo-atomic molecule

"A molecule which is composed of same or one kind of atoms is called a homo-atomic molecule or elemental molecule"

Examples: O_2, O_3, P_4, S_8 etc.

(b) Hetero-atomic molecule

"A molecule which is composed of different types of atoms is called a hetero-atomic molecule or compound molecule"

Examples: CO, SO_2, NH_3, CH_4 etc.

Atomicity

"The number of atoms present in a molecule is called atomicity."

Substance	Molecule	Atomicity
Helium	He	1
Water	H_2O	3
Glucose	$C_6H_{12}O_6$	24
Sucrose	$C_{12}H_{22}O_{11}$	45

(ii) On the basis of atomicity

On the basis of atomicity, molecules are of two types.

(a) Mono-atomic molecule

(b) Polyatomic molecule

(a) Mono-atomic molecule

"The molecule which consists of only one atom is called mono-atomic molecule."

Examples Noble gases (He, Ne, Ar, Kr, Xe and Rn) has monoatomic molecules

(b) Polyatomic molecule

"A molecule which consists of two or more, same or different kinds of the atoms is called a polyatomic molecule."

Examples CO, CO_2, O_2, O_3, $C_6H_{12}O_6$ etc.

(It can be diatomic, tri-atomic, tetra-atomic)

(iii) On the basis of size of molecule

On the basis of size, molecules are of two types.

(a) Micromolecules

They are small in size. They are simple molecules and exist as monomer

Examples H_2O, CO_2, C_6H_6 etc.

(b) Macromolecules

They are large in size having large number of atoms.

Examples Haemoglobin, cellulose, starch, graphite etc.

Haemoglobin

- It is a blood protein.
- It transports oxygen from our lungs to all parts of the body.
- Each molecule of haemoglobin is made up of nearly 10,000 atoms.
- It is 68,000 times heavier than a hydrogen atom.
- It contains carbon, hydrogen, nitrogen, oxygen and iron

Q. How many times a He atom is lighter than a haemoglobin molecules?
(a) 68000
(b) 34000
(c) 17000
(d) 1000

Difference between Atom and Molecule

ATOM	MOLECULE
1) It is the smallest particle of an element.	1) It is the smallest particle of a pure substance.
2) It is represented by a symbol.	2) It is represented by molecular formula.
3) It shows the properties of element.	3) It shows the properties of the substance.
4) It retains its identity in a chemical reaction.	4) It does not retain its identity in a chemical reaction.
5) It cannot be further sub-divided by ordinary chemical reactions	5) It can be further sub-divided by ordinary chemical reaction.
6) It may or may not exist in free state.	6) It can exist in free state.

Ion

"Those species which carry either positive or negative charge are called ions."

Types There are two types of ion

(i) Positive ion or cation.

(ii) Negative ion or anion.

Cations and Anions: During electrolysis, the negative electrode or cathode attracts positive ions, called **cations**. The positive electrode or anode attracts negative ions, called **anions**.

(i) Positive Ion

"It is that ion which is carrying a positive charge. A positive ion is formed when an atom loses one or more electrons."

$$A \longrightarrow A^+ + e^-$$

- A positive ion is also called a cation.
- A positive ion may carry +1, +2 or +3 charge depending upon the number of electrons lost by the atom.
- We have to supply sufficient amount of energy in order to remove an electron from the valence shell of an atom. It means the formation of a positive ion is an endothermic process.
- Formation of cation is an oxidation process.
- Metal atom can easily lose electrons to form positive ions like Na^+, K^+, Ca^{2+} and Fe^{3+} ions.
- Size of a cation is smaller than its parent atom.

$$\underset{186\ pm}{Na} \longrightarrow \underset{95\ pm}{Na^{1+}} + 1e^-$$

Q. The formation of positive ion is an endothermic process. Justify.

(ii) Negative ion

"It is that ion which is carrying a negative charge. A negative ion is formed when an atom gains one or more electrons."

$$B + e^- \longrightarrow B^-$$

- A negative ion is also called an anion.

- A negative ion may carry −1, −2 or −3 charge depending upon the number of electrons gained by the atom.
- Energy is released when one electron is added in the valence shell of an isolated neutral atom. It means that the formation of an uni-negative ion is an exothermic process while formation of di-negative ion is an endothermic process.
- Non-metals mostly gain electrons and to form negative ions like F^{-1}, Cl^{-1}, S^{2-} and O^{2-} ions etc.
- Formation of anion is a reduction process.

These cations and anions have entirely different properties from their parent atoms.

- Size of anion is larger than its parent atom.

$$\underset{99\ pm}{Cl} + 1e^- \longrightarrow \underset{181\ pm}{Cl^-}$$

Q. Justify that formation of di-negative ion is an endothermic process

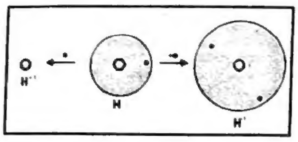
Polyatomic ions

These are the positive or negative ions which consist of group of atoms.

- The positive polyatomic ions are less common. For example, NH_4^+ ions and certain carbocations in organic chemistry.
- There are many examples of negative polyatomic ions like OH^-, CO_3^{2-} and SO_4^{2-} ions PO_4^{3-}, MnO_4^{1-}, $Cr_2O_7^{2-}$ etc.

Difference between Cation and Anion

Cation (positive ion)	Anion (negative ion)
• A cation is formed by the loss of electron or electrons from a neutral atom. $A \rightarrow A^+ + 1e^-$	• Anion is form by the gain of electron or electrons by a neutral atom. $B + 1e^- \rightarrow B^-$
• Formation of cation is an endothermic process. $Na_{(g)} \longrightarrow Na^+_{(g)} + 1e^-$ $\Delta H = +496\ kJ\ mol^{-1}$	• Formation of uninegative ion is an exothermic process whereas the formation of dinegative ion is an endothermic process. $O_{(g)} + 1e^- \longrightarrow O^-_{(g)}$ $\Delta H = -141\ kJ\ mol^{-1}$ $O^-_{(g)} + 1e^- \longrightarrow O^{2-}_{(g)}$ $\Delta H = +780\ kJ\ mol^{-1}$
• Formation of cation is an oxidation process.	• Formation of anion is a reduction process.
• The size of cation is smaller than its parent atom. e.g. $\underset{186\ pm}{Na_{(g)}} \longrightarrow \underset{95\ pm}{Na^+_{(g)}} + 1e^-$	• The size of anion is greater than its parent atom. e.g. $\underset{99\ pm}{Cl_{(g)}} + 1e^- \longrightarrow \underset{181\ pm}{Cl^-_{(g)}}$
• The behaviour of neutral atom and cation is different.	• The behaviour of neutral atom and anion is different.
• Usually, electropositive metals lose electrons and form cations.	• Usually, non-metals gain electrons and form anions.
• The charge on cations is equal to number of electrons lost. e.g., $Na \longrightarrow Na^+ + 1e^-$ $Ca \longrightarrow Ca^{2+} + 2e^-$ $Al \longrightarrow Al^{3+} + 3e^-$	• The charge on anions is equal to number of electrons gained e.g., $Cl + 1e^- \longrightarrow Cl^-$ $O + 2e^- \longrightarrow O^{2-}$ $N + 3e^- \longrightarrow N^{3-}$



Molecular Ion

"Those ions which are produced by the removal of one or more electron or electrons from the molecule of a substance are called molecular ions."

Types There are two types of molecular ion.

(a) Cationic molecular ions

They have positive charge. They are more abundant than anionic molecular ions.

Example N_2^+, CO^+, CH_4^+ etc.

(b) Anionic molecular ions

They have negative charge. They are less abundant.

Example O_2^{2-}, N_2^- etc.

MCQ's
Which of the following is not a molecular ion?
(a) CH_4^+ (b) NH_4^+
(c) O_2^{1-} (d) NH_3^+

Formation

These ions can be generated by **passing high energy electron beam as α – particles** or X – rays through a gas.

Application

The breakdown of molecular ions obtained **from the natural products can give important information about their** structure.

Q.4 What are ions? Under what conditions are they produced?

Ans. Ions

"Those species which carry either positive or negative charge are called ions."

Formation of ions

Ions are formed under following conditions

(i) By passing different radiations through gaseous mixture.

(ii) By adding the substance into an aqueous solution.

(iii) By heating the substance (in molten state).

Prove that : 1amu = 1.661×10^{-27} kg

Solution :

6.02×10^{23} C atom = 12g

1 C atom = $\frac{12}{6.02\times10^{23}}$ g

1 C atom = 1.99×10^{-23} g

$\frac{1}{12^{th}}$ of carbon atom = $\frac{1.99\times10^{-23}}{12}$ g

= 1.661×10^{-24} g

= 1.661×10^{-27} kg

Relative Atomic Mass

"It is the mass of an atom of an element as compared to the mass of an atom of carbon taken as 12."

- The term atomic mass is preferred over atomic weight because mass is more fundamental unit than weight.
- Atomic mass is a relative term. It tells us how much heavier or lighter an atom of the element is, than an atom of carbon – 12.
- Carbon – 12 is used as a standard because it is stable and exist abundantly.

Relative Atomic Masses of a Few Elements

Element	Relative Atomic Mass (amu)	Element	Relative Atomic Mass (amu)
H	1.008	Cl	35.453
O	15.9994	Cu	63.546
Ne	20.1797	U	238.0289

Atomic Mass Unit

"1/12th of the mass of one atom of carbon–12 is called the atomic mass unit. It is abbreviated as amu."

$$1\ amu = 1.661\times10^{-27}\ kg = 1.661\times10^{-24}\ g = 1.661\times10^{-21}\ mg$$

Q. Which one of the following is the relative atomic mass of an element?

(a) $\frac{\text{average mass of one atom of the element}}{\text{mass of one atom of } ^1H}$

(b) $\frac{\text{average mass of one atom of the element}}{\text{mass of one atom of } ^{12}C}$

(c) $\frac{\text{average mass of one atom of the element}}{\frac{1}{12}\times\text{average mass of one atom of carbon}}$

(d) $\frac{\text{average of mass of one atom of the element}}{\frac{1}{12}\times\text{mass of one atom of } ^{12}C}$

Isotopes

"Atoms of the same element which have the same atomic number but different mass numbers due to difference in the number of neutrons are called isotopes of that element."

The phenomenon of isotopy was first discovered by Soddy.

Examples

- **Isotopes of hydrogen**

Hydrogen consists of three isotopes which are protium (^1_1H), deuterium (^2_1H) and tritium (^3_1H). All these isotopes have the same atomic number i.e one, but they have different mass numbers 1, 2 and 3 respectively.

- **Isotopes of carbon**

Carbon also consists of three isotopes which are C–12 ($^{12}_6C$), C–13 ($^{13}_6C$) and C–14 ($^{14}_6C$). All these isotopes have the same atomic number i.e., six but they have different mass numbers 12, 13 and 14 respectively.

Oxygen has three, nickel has five, calcium has six, palladium has six, cadmium has nine and tin has eleven isotopes. The elements like arsenic, fluorine, iodine and gold etc have only a single isotope. They are called mono – isotopic elements.

Isobars:
Those atoms which have the same mass numbers but different atomic numbers. ^{14}C, ^{14}N.

Isoelectronic species:
Those species i.e atoms, ions or molecules which have the same number of electrons are called iso-electronic species e.g. Ne, Mg^{2+}, O^{2-} are isoelectronic species.

Isotones:
Atoms of the different elements having same number of neutrons but different mass numbers are called isotones. e.g. $^{30}_{14}Si$, $^{31}_{15}P$, $^{32}_{16}S$ are isotones.

Similarities and Dissimilarities of Isotopes of an Element

Similarities	Dissimilarities
Isotopes of an element have same • Atomic number • Number of proton • Number of electron • Chemical properties due to same electronic configuration • Position in modern periodic table	Isotopes of an element have different • Atomic mass • Number of neutron • Radioactive properties due to different composition of nuclei • Physical properties • Half life due to different stabilities

Relative abundance of isotopes

"The percentage of each isotope in a mixture of isotopes of an element is called relative abundance."

- Different isotopes have their own natural abundance.
- The relative abundance of isotopes is measured by mass spectrometry.

- The properties of a particular element, which are mentioned in the literature, mostly correspond to the most abundant isotope of that element

Natural Abundance of Some Common Isotopes

Element	Isotope	Abundance (%)	Mass (amu)
Hydrogen	^{1}H , ^{2}H	99.985, 0.015	1.007825, 2.01410
Carbon	^{12}C , ^{13}C	98.893, 1.107	12.0000, 13.00335
Nitrogen	^{14}N , ^{15}N	99.634, 0.366	14.00307, 15.00011
Oxygen	^{16}O , ^{17}O, ^{18}O	99.759, 0.037, 0.204	15.99491, 16.99914, 17.9916
Sulphur	^{32}S , ^{33}S , ^{34}S , ^{36}S	95.0, 0.76, 4.22, 0.014	31.97207, 32.97146, 33.96786, 35.96709
Chlorine	^{35}Cl , ^{37}Cl	75.53, 24.47	34.96885, 36.96590
Bromine	^{79}Br , ^{81}Br	50.54, 49.49	78.918, 80.916

The distribution of isotopes among the elements varied and complex as it is evident from above table.

Occurrence of Isotopes

At present more than 280 different isotopes occur in nature.

- **40** radioactive isotopes are also included in this number **(280)**.
- Almost **300** unstable radioactive isotopes of different elements have been produced by the artificial disintegration.
- In general elements with odd atomic number almost never possess more than two stable isotopes.
- The elements of even atomic number usually have larger number of isotopes.
- The isotopes whose mass numbers are multiple of four are particularly abundant. For example **^{16}O, ^{24}Mg, ^{28}Si, ^{40}Ca** and **^{56}Fe**. These isotopes exist abundantly and form about **50%** of the earth crust.
- Out of **280** isotopes that occur in nature, **154** isotopes have even atomic number and even mass number.

Q. Why isotopes have identical chemical properties but different physical properties?

Ans. The chemical properties of a substance depends upon its outer shell electronic configuration. Since isotopes of an element have same electronic configuration, so they show similar chemical properties.

e.g., $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

$D_2 + \frac{1}{2}O_2 \rightarrow D_2O$

Moreover, due to different **nuclear composition physical properties of isotopes are different.**

DETERMINATION OF RELATIVE ATOMIC MASS OF ISOTOPES BY MASS SPECTROMETRY

Mass Spectrometer

"It is an instrument which is used to measure the exact masses of different isotopes of an element along with their relative abundance."

Q. Write down principle of mass spectrometry.

Principle of mass spectrometry

In this technique, a substance is first volatilized and then ionized with the help of high energy beam of electrons. The gaseous positive ions, thus formed, are separated on the basis of their mass to charge ratio (m/e) and then recorded in the form of peaks.

- **Aston's mass spectrograph**

First mass spectrograph was designed by Aston in 1919. It was designed for the identification of isotopes of an element on the basis of their atomic masses.

- **Dempster's mass spectrometer**

It was designed for identification of elements which were available in solid state.

Determination of Relative Atomic Masses of Isotopes by Dempster's Mass Spectrometer

Different steps involved in the determination of exact atomic masses and the relative abundances of different isotopes of an element are given below

The need for a vacuum

The space inside a mass spectrometer is connected to a vacuum pump. The ions under study must be able to move freely. The mass spectrometer would not work properly if the ions collided with the molecules (O_2 & N_2) present in the atmosphere.

(i) Vapourization

The substance whose analysis for the separation of isotopes is required, is converted into the vapour state. The pressure of these vapours is kept very low, that is, 10^{-6} to 10^{-7} torr

(ii) Ionization

These vapours are then allowed to enter the ionization chamber where fast moving electrons are thrown upon them. The atoms of isotopic element present in the form of vapours, are ionized. These positively charged ions of isotopes of an element have different masses depending upon the nature of the isotopes present in them

Q. How the ions in the mass spectrometer are accelerated and deflected?

(iii) Acceleration

The positive ions of each isotope has its own (m/e) value. When a potential difference (E) of 500-2000 volts is applied between perforated accelerating plates, then these positive ions are strongly attracted towards the negative plate. In this way, the ions are accelerated.

(iv) Deflection

The beam of accelerated positive ions is then allowed to pass through a strong magnetic field of the strength H. This magnetic field is applied in a direction which is perpendicular to the path of the positive ions. The applied magnetic field will help us in the separation of positive ions on the basis of their m/e values. The magnetic field makes the ions to move in a circular path. The ions of definite m/e value will move in the form of groups one after the other and fall on the electrometer.

If an element exists as diatomic molecules i.e. Cl_2, O_2, H_2 etc. then the spectrum will contain peaks both for the separate atoms and for the molecules. e.g. the mass spectrum of chlorine will have peaks for Cl^+, with $\frac{m}{e}$ values of 35 and 37 and peaks for Cl_2^+ with $\frac{m}{e}$ values of 70, 72 and 74.

(v) Mathematical explanation

The mathematical relationship between m/e values and deflection in the circular path is

$$m/e = H^2 r / E$$

Where, H = strength of magnetic field

E = Strength of electric field

r = Radius of circular path

If E is increased, by keeping H constant then radius will increase and positive ion of a particular m/e will fall at a different place as compared to the first place. This can also be done by changing the magnetic field. Smaller the (m/e) of an isotope, smaller the radius of curvature produced by the magnetic field according to above equation. Each ion sets up a minute electrical current.

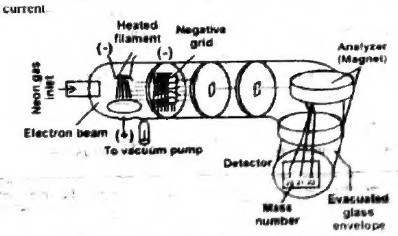


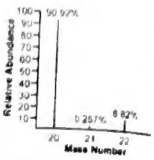
Diagram of a simple mass spectrometer

(vi) Electrometer (Ion collector)

Electrometer develops the electrical current. The strength of the current thus measured gives the relative abundance of ions of a definite m/e value.

(vii) Comparison with Carbon–12

Similarly, the ions of other isotopes having different masses are made to fall on the collector and the current strength is measured. The current strength in each case gives the relative abundance of each of the isotopes. The same experiment is performed with C-12 isotope and the current strength is compared. This comparison allows us to measure the exact mass number of the isotope.



Computer plotted graph for the isotopes of neon.

Modern Spectrograph

In modern spectrographs, each ion strikes a detector, the ionic current is amplified and is fed to the recorder. The recorder makes a graph showing the relative abundance of isotopes plotted against the mass number.

Separation of Isotopes

Since isotopes of an element have same chemical properties, so they cannot be separated by chemical methods. Following physical methods are used for their separation

1. Gaseous diffusion
2. Thermal diffusion
3. Distillation
4. Ultracentrifuge
5. Electromagnetic separation
6. Laser separation

Q.5 (a) How do you deduce the fractional atomic masses of elements from the relative isotopic abundance? Give two examples in support of your answer.

Average Atomic Masses

"The mass of an element which is obtained from isotopic mass and relative abundance of its isotopes is called average atomic mass"

Example # 1

A sample of neon is found to consist of $^{20}_{10}Ne$, $^{21}_{10}Ne$, $^{22}_{10}Ne$ in the percentages of 90.92%, 0.26% and 8.82% respectively. Calculate the fractional atomic mass of neon.

Solution

The overall atomic mass of neon is the average of the determined atomic masses of individual isotopes. Hence,

$$\text{Average atomic mass} = \frac{20\times 90.92 + 21\times 0.26 + 22\times 8.82}{100} = 20.18\,\text{amu}$$

Hence, the average atomic mass of neon is 20.18 amu

It is important to realize that no individual neon atom has a mass of 20.18 amu. For most laboratory purposes, however, we consider the sample to consist of atoms with this average atomic mass.

Example # 2

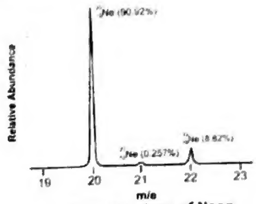
Chlorine has two isotopes $^{35}_{17}Cl$, $^{37}_{17}Cl$ having percentage existence as 75.53% and 24.47% respectively. Calculate average atomic mass of Cl.

Solution

$$\text{Average atomic mass} = \frac{35\times 75.53 + 37\times 24.47}{100} = 35.489\,\text{amu}$$

Q5b. How does a mass spectrograph show the relative abundance of isotopes of an element?

Ans. A mass spectrograph gives result in the form of a mass spectrum. Actually mass spectrum is a plot of data in such a way that (m/e) of an isotope is plotted as abscissa (X-axis) and relative number of ions as ordinate (Y-axis).



Mass spectrum of Neon

- Height of peaks in the graph is proportional to relative natural abundance of isotope of an element.
- Number of Peaks gives number of possible isotopes.

Q5c. What is the justification of two strong peaks in the mass spectrum for bromine; while for iodine only one peak at 127 amu is indicated?

Ans. In mass spectrum height of peaks indicates relative abundance of isotope of an element where as number of peaks gives us number of possible isotopes of that element.

In case of **bromine**, we observe two strong peaks of almost equal heights. It shows that Br has two naturally occurring isotopes i.e., ^{79}Br and ^{81}Br with a relative abundance of 50.54% and 49.46% respectively

On the other hand **iodine** being mono isotopic ^{127}I gives only one peak at 127 amu (atomic mass of iodine)

Q6. Silver has atomic number 47 and has 16 known isotopes but two occur naturally i.e. Ag-107 and Ag-109. Given the following mass spectrometric data, calculate the average atomic mass of silver.

Isotopes	mass (amu)	Percentage abundance
^{107}Ag	106.90509	51.84
^{109}Ag	108.90476	48.16

Ans. Given data

Mass of ^{107}Ag = 106.90509 amu
Mass of ^{109}Ag = 108.90476 amu
Percentage of ^{107}Ag = 51.84%
Percentage of ^{109}Ag = 48.16%

Required

Average atomic mass of Ag = ?

Solution

$$\text{Average atomic mass of Ag} = \frac{(\text{Isotopic mass of }^{107}Ag \times \%\text{ of }^{107}Ag) + (\text{Isotopic mass of }^{109}Ag \times \%\text{ of }^{109}Ag)}{100}$$

$$= \frac{(106.90509 \times 51.84) + (108.90476 \times 48.16)}{100}$$

$$= \frac{5541.96 + 5244.85}{100}$$

$$= \frac{10786.81}{100}$$

Average atomic mass of Ag = 107.87 amu

Q7. Boron with atomic number 5 has two naturally occurring isotopes. Calculate the percentage abundance of ^{10}B and ^{11}B from the following information

Average Atomic mass of Boron	= 10.81 amu
Isotopic mass of ^{10}B	= 10.0129 amu
Isotopic mass of ^{11}B	= 11 0093 amu

Ans. Given data

Average Atomic mass of Boron	= 10.81 amu
Isotopic mass of ^{10}B	= 10 0129 amu
Isotopic mass of ^{11}B	= 11 0093 amu

Required

Percentage abundance of ^{10}B = ?

Percentage abundance of ^{11}B = ?

Solution

Suppose

Percentage abundance of ^{10}B = x

Percentage abundance of ^{11}B = (100 – x)

$$\text{Average Atomic mass of boron} = \frac{(\text{Isotopic mass of } ^{10}B \times \% \text{ of } ^{10}B) + (\text{Isotopic mass of } ^{11}B \times \% \text{ of } ^{11}B)}{100}$$

Putting the values

$$10.81 = \frac{(10.0129 \times x) + \{11.0093 \times (100 - x)\}}{100}$$

$$10.81 \times 100 = (10.0129x) + (1100.93 - 11.0093x)$$

$$1081 - 1100.93 = 10.0129x - 11.0093x$$

$$-19.93 = -0.9964x$$

$$\frac{-19.93}{-0.9964} = x$$

$$x = 20.002\%$$

Percentage abundance of ^{10}B = **20.002%**

Percentage abundance of ^{11}B = 100 – 20.002 = **79.998%**

DETERMINATION OF PERCENTAGE OF ELEMENTS IN A COMPOUND

The percentage of an element in a compound is the number of grams of that element present in 100 grams of the compound, and is calculated as

$$\textbf{Percentage of an element} = \frac{\textbf{Mass of element in the compound}}{\textbf{Formula mass of the compound}} \times 100$$

Empirical Formula

"A chemical formula which shows the simplest whole number ratio between the atoms of different elements present in a compound is called empirical formula."

Examples

Substance	Empirical formula
Glucose	CH_2O
Benzene	CH
Water	H_2O
Sodium Chloride	NaCl

Steps involved in determination of empirical formula

The following steps are involved in the determination of empirical formula

1) Determination of the percentage composition

$$\textbf{\% of an element} = \frac{\textbf{mass of the element}}{\textbf{molar mass of compound}} \times 100$$

2) Finding the number of gram atoms of each element. For this purpose divide the percentage of an element by its atomic mass

$$\textbf{Number of gram atoms (moles)} = \frac{\textbf{\% of an element}}{\textbf{atomic mass}}$$

3) Determination of the atomic ratio of each element To get this, divide the number of moles of each element (gram atoms) by the smallest number of moles

$$\textbf{Atomic ratio} = \frac{\textbf{number of moles}}{\textbf{smallest number of moles}}$$

4) If the atomic ratio is simple whole number, it gives the empirical formula, otherwise multiply with a suitable digit to get the whole number atomic ratio

EMPIRICAL FORMULA FROM COMBUSTION ANALYSIS

Combustion Analysis

"The analysis which is made to determine the amounts of different elements present in a compound by burning a known amount of organic compound containing C, H and O in the presence of oxygen is called combustion analysis"

Q. Combustion analysis is used to determine?
(a) %age composition
(b) Empirical formula
(c) Molecular formula
(d) All of these

Sole Product

$CO_{2(g)}$ and $H_2O_{(g)}$ are sole (main) products during combustion of an organic compound

Procedure

A weighed sample of the organic compound is placed in the combustion tube. This combustion tube is fitted in a furnace Oxygen is supplied to burn the organic compound. Hydrogen is converted into H_2O and carbon is converted into CO_2

H_2O absorber

Next to combustion tube there is H_2O absorber chamber It contains $Mg(ClO_4)_2$ which absorbs H_2O produced during combustion

CO_2 absorber

After H_2O absorber chamber, next is the CO_2 absorber chamber. It contains 50% KOH which absorbs CO_2 produced during combustion

The difference in the amounts or masses of these absorbers gives us the amounts of H_2O and CO_2 produced

Combustion analysis

Calculations

$$\textbf{\% of Carbon} = \frac{\text{Mass of } CO_2}{\text{Mass of organic compound}} \times \frac{12.00}{44.00} \times 100$$

$$\%\ of\ Hydrogen = \frac{Mass\ of\ H_2O}{Mass\ of\ organic\ compound} \times \frac{2.016}{18} \times 100$$

The percentage of oxygen is obtained by the **method of difference.**

% of Oxygen = **100 − (% of carbon + % of hydrogen)**

Molecular Formula

"A formula which gives the total number of atoms of different elements present in the molecule of a compound is called molecular formula."

Examples

Substance	Molecular Formula
Water	H_2O
Benzene	C_6H_6
Glucose	$C_6H_{12}O_6$
Sulphuric acid	H_2SO_4

Q. Why some compounds have same empirical and molecular formula?

Relationship between empirical and molecular formula

1) A compound may have same empirical and molecular formula. For example, CH_4, H_2O, CO_2, NH_3, $C_{12}H_{22}O_{11}$ are the empirical and molecular formulas of the respected compounds. For such compounds the value of "n" is unity (1).
2) The molecular formula may be integral multiple of empirical formula. For example, Molecular formula of glucose is $C_6H_{12}O_6$ which is six times the empirical formula of glucose (CH_2O). The molecular formula of benzene is C_6H_6 which is six times the empirical formula of benzene (CH). So molecular formula is related to empirical formula as

Molecular formula = n × Empirical formula

3) A compound may have empirical formula but no molecular formula. For example, sodium chloride has the empirical formula NaCl but no molecular formula. All the ionic compounds have empirical formula but no molecular formula.
4) Molecular compounds having same molecular formula are called isomers e.g. ethyl alcohol or dimethyl ether have same molecular formula C_2H_6O.

DIFFERENCE BETWEEN EMPIRICAL AND MOLECULAR FORMULA

Empirical formula	Molecular formula
• A chemical formula which shows the simplest whole number ratio between the atoms of different elements present in a compound is called empirical formula.	• A formula which gives the total number of atoms of different elements present in the molecule of a compound is called molecular formula.
• Empirical formula can be determined directly by different methods e.g., combustion analysis, elemental analysis etc.	• Molecular formula can never be determined directly. It is determined as follows: Molecular formula = n × (Empirical formula)
• Empirical formula is used for all compounds.	• Molecular formula is used for only molecular compounds.
Examples Empirical formula of glucose = CH_2O Empirical formula of water = H_2O	**Examples** Molecular formula of glucose = $C_6H_{12}O_6$ Molecular formula of water = H_2O

Q8. Define the following terms and give three examples of each

(i) Gram atom **(v) Molar volume** **(ii) Gram molecular mass**
(vi) Avogadro's number **(iii) Gram formula** **(vii) Stoichiometry**
(iv) Gram ion

CONCEPT OF MOLE

Gram Atom

"Atomic mass of an element expressed in grams is called a gram atom. It is also called one gram mole or simply a mole of that element."

Particle

A single particle of a substance may refer to an atom, a molecule, an ion, an electron or to any identifiable particle. Chemists refer to a collection of particles as **chemical species**

Formula

$$\text{Number of gram atoms or mole of an element} = \frac{\text{Mass of element in grams}}{\text{Atomic mass of an element}}$$

Examples

(i) 1 gram atom of hydrogen = 1.008 g
(ii) 1 gram atom of carbon = 12.000 g
(iii) 1 gram atom of uranium = 238.0 g

Gram Molecule

"Molecular mass of a compound expressed in grams is called gram molecule or gram mole or simply the mole of a substance."

Formula

$$\text{Number of gram molecules or moles of a molecular substance} = \frac{\text{Mass of the molecular substance in grams}}{\text{Molecular mass of the substance}}$$

Examples

(i) 1 gram molecule of water = 18.0 g
(ii) 1 gram molecule of H_2SO_4 = 98.0 g
(iii) 1 gram molecule of sucrose 342.0 g

Gram Formula

"The formula mass of an ionic compound expressed in grams is called gram formula of the substance. It is also called gram mole or simply mole."

Formula

$$\text{Number of gram formulas or moles of ionic substance} = \frac{\text{Mass of the ionic substance grams}}{\text{Formula mass of the ionic substance}}$$

Examples

(i) 1 gram formula of NaCl = 58.50 g
(ii) 1 gram formula of Na_2CO_3 = 106.0 g
(iii) 1 gram formula of $AgNO_3$ = 170.0 g

Gram Ion

"Ionic mass of an ionic specie expressed in grams is called one gram ion or one mole of ions."

Formula

$$\text{Number of gram ions or moles of ionic specie} = \frac{\text{Mass of ionic specie in grams}}{\text{Formula mass of the ionic specie}}$$

Examples

(i) 1 gram formula of OH^- = 17 g
(ii) 1 gram ion of SO_4^{2-} = 96 g
(iii) 1 gram ion of CO_3^{2-} = 60 g

Mole

"When the atomic mass of an element, molecular mass of a molecular substance, formula mass of an ionic compound or ionic mass of an ionic species is expressed in grams then it is called **mole**."

or

"The amount of a substance which contains Avogadro's number of particles (atoms, molecules, formula units, or ions) is called **mole**."

> The word 'mole' was introduced around [illegible] by Wilhelm Ostwald who derived the term from Latin word moles meaning a 'heap' or 'pile'

- It is denoted by "n".
- It is abbreviated as "mol".
- It is the SI unit of measuring the quantity of substance.

$$n = \frac{m}{M}$$

Examples

Element	1 mole of Na	= 23 g
Molecular compound	1 mole of H_2O	= 18 g
Ionic compound	1 mole of NaCl	= 58.5 g
Ionic specie	1 mole of HCO_3^{-1}	= 61 g

Formula

$$\text{Mole} = \frac{\text{Given mass of the substance}}{\text{Atomic mass / Molecular mass / Formula mass}}$$

$$\text{Mole} = \frac{\text{Given mass of the substance}}{\text{Molar mass}}$$

> **A mole of substance represents:**
> - 6.023×10^{23} particles
> - 22.4 L of gas at STP
> - 1 gram atom of an element
> - 1 gram molecular mass of a substance
> - 1 gram formula mass of an ionic substance

Avogadro's Number

"The number of particles (atoms, molecules, formula units or ions) which are present in one mole of a substance is called Avogadro's number."

or

"The number of atoms, molecules or ions in one gram atom of an element, one gram molecule of a compound and one gram ion of a substance, respectively is called Avogadro's number."

Symbol It is represented by "N_A"
Value It's value is 6.022×10^{23}
Unit It's unit is mol^{-1}.

Examples

1 mole of Na = 23 g = 6.022×10^{23} atoms
1 mole of H_2SO_4 = 98 g = 6.022×10^{23} molecules
1 mole of $CaCl_2$ = 111 g = 6.022×10^{23} formula units
1 mole of OH^- = 17 g = 6.022×10^{23} ions

> **Q. What is the mass of one molecule of water?**
> (a) $\frac{6.0\times10^{23}}{18}$ g
> (b) $\frac{6.0}{18}\times10^{-23}$ g
> (c) $\frac{18}{6.0\times10^{23}}$ g
> (d) $\frac{1}{6.0\times18\times10^{23}}$ g

> **Q. Which of the following contains the largest number of atoms?**
> (a) 8g of methane
> (b) 15g of hydrogen fluoride
> (c) 15.6g of benzene
> (d) 21.8g of bromoethane

Relationships

The relationships between amounts of substances in term of their masses and number of particles present in them are

1) **Number of atoms of an element** $= \frac{\text{Mass of the element}}{\text{Atomic mass}} \times N_A$

2) **Number of molecules of a compound** $= \frac{\text{Mass of compound}}{\text{Molecular mass}} \times N_A$

3) **Number of ions of ionic specie** $= \frac{\text{Mass of the ion}}{\text{Ionic mass}} \times N_A$

Q9. (a) 23 g of sodium and 238 g of uranium have equal number of atoms in them.

Ans. Sodium and uranium both are elements. 23g & 238g are the molar masses of sodium & uranium respectively

23g of Na = 1 mol

238 g of uranium = 1 mol

According to definition of Avogadro's number, 1 mol of all the elements have same number of atoms in them i.e., 6.02×10^{23}. Therefore

23 g of sodium = 1 mol = 6.02×10^{23} sodium atoms

238 g of uranium = 1 mol = 6.02×10^{23} uranium atoms

Q9 (b) Mg atom is twice heavier than that of carbon atom.

Ans. We know the molar masses of each element i.e.

Mg e P Net
1 mol of magnesium = 24 g = 6.02×10^{23} magnesium atoms 24g 12 12 12

1 mol of carbon = 12 g = 6.02×10^{23} carbon atoms

By this information, we can calculate the mass of each magnesium and carbon atom by dividing molar masses with Avogadro's number as follows carbon 6 6 6 12

6.02×10^{23} magnesium atoms has mass = 24 g

1 magnesium atom has mass $= \frac{24\ g}{6.02\times10^{23}}$

$= 3.9867 \times 10^{-23}$ g

1U = 238
1 Na = 23
1 mole 6.02×10^{23}

Similarly,

6.02×10^{23} carbon atoms has mass = 12 g

1 carbon atom has a mass $= \frac{12}{6.02\times10^{23}}$

$= 1.9933 \times 10^{-23}$ g

By comparing both masses

Mg	:	C
3.9867×10^{-23} g	:	1.9933×10^{-23} g

Simplify them

$\frac{3.9867\times10^{-23}}{1.9933\times10^{-23}}$	:	$\frac{1.9933\times10^{-23}}{1.9933\times10^{-23}}$
2	:	1

We can easily conclude that magnesium atom is twice heavier in mass than that of a carbon atom.

Q9. (c) 180 g of glucose and 342 g of sucrose have same number of molecules but different number of atoms present in them.

Ans. Molar mass of glucose ($C_6H_{12}O_6$) = 180 g mol^{-1}

Molar mass of sucrose ($C_{12}H_{22}O_{11}$) = 342 g mol^{-1}

Both glucose and sucrose are molecular species. Therefore one mole contains same number of molecules i.e., Avogadro's number (6.02×10^{23}).

180 g of glucose = 1 mol = 6.02×10^{23} molecules of glucose

342 g of sucrose = 1 mol = 6.02×10^{23} molecules of sucrose

One molecule of glucose has different number of atoms than one molecule of sucrose so one mole of each molecule contains different number of atoms in them.

As 1 molecule of glucose contains = 24 atoms

So 1 mole glucose molecules contain = $24 \times 6.02 \times 10^{23}$ atoms

Similarly

As 1 molecule of sucrose contains = 45 atoms

So 1 mole sucrose molecules contain = $45 \times 6.02 \times 10^{23}$ atoms

Qs. (d) 4.9 g of H_2SO_4 when completely ionized in water, have equal number of positive and negative charges but the number of positively charged ions are twice the number of negatively charged ions.

Ans. Given data

Mass of H_2SO_4 = 4.9 g

Required

Number of H^+ = ?

Number of SO_4^{2-} ions = ?

Total positive charge = ?

Total negative charge = ?

Solution

(i) Firstly we calculate number of moles

Number of moles of $H_2SO_4 = \dfrac{\text{Mass in grams}}{\text{Molar mass}}$

Molar mass of H_2SO_4 = 98 g mol^{-1}

So number of moles $= \dfrac{4.9\ g}{98\ g\ mol^{-1}} = 0.05$ moles

(ii) Now calculate molecules of H_2SO_4

Number of molecules of H_2SO_4 = Number of moles of $H_2SO_4 \times N_A$

$= 0.05 \times 6.02 \times 10^{23}$

$= 3.01 \times 10^{22}$ molecules

(iii) Ionization of H_2SO_4 in water

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

Now we can calculate

Total positive ions

H_2SO_4	:	H^+
1	:	2
3.01×10^{22}	:	$2 \times 3.01 \times 10^{22}$
		6.02×10^{22} ions

Total negative ions

H_2SO_4	:	SO_4^{2-}
1	:	1
3.01×10^{22}	:	3.01×10^{22} ions

Comparison of H^+ and SO_4^{2-}

H^+	:	SO_4^{2-}
6.02×10^{22}	:	3.01×10^{22}
$\dfrac{6.02 \times 10^{22}}{3.01 \times 10^{22}}$	:	$\dfrac{3.01 \times 10^{22}}{3.01 \times 10^{22}}$
2		1

- So number of positive ions are twice than that of negative ions

Total positive charge

Number of positive ions × charge on one positive ion

$= 6.02 \times 10^{22} \times (+1)$

$= +6.02 \times 10^{22}$

Total negative charge

Number of negative ions × charge on one negative ion

$= 3.01 \times 10^{22} \times (-2)$

$= -6.02 \times 10^{22}$

- So charges are same

(e) One mg of K_2CrO_4 has thrice the number of ions than the number of formula units when ionized in water.

Ans. Given data

Mass of K_2CrO_4 = 1 mg = 10^{-3} g

Required

Total ions of K_2CrO_4 = ?

Solution

Molar mass of K_2CrO_4 = 194 g mol^{-1}

Number of moles of $K_2CrO_4 = \dfrac{\text{Mass in grams}}{\text{Molar mass}}$

$= \dfrac{10^{-3}\ g}{194\ g\ mol^{-1}} = 5.15 \times 10^{-6}$ moles

Total formula units of K_2CrO_4 = Number of moles of $K_2CrO_4 \times N_A$

$= 5.15 \times 10^{-6} \times 6.02 \times 10^{23}$

$= 3.10 \times 10^{18}$ formula units

In water, K_2CrO_4 ionizes as

$$K_2CrO_4 \rightleftharpoons 2K^+ + CrO_4^{-2}$$

1 formula unit of K_2CrO_4 produces ions = 3

3.10×10^{18} formula units of K_2CrO_4 produce ions $= 3 \times 3.10 \times 10^{18}$

$= 9.30 \times 10^{18}$ ions

So one mg of K_2CrO_4 produces thrice the number of ions than the number of formula units.

Molar Mass

"The mass of one mole of a substance is called molar mass."

Unit Its unit is g/mole.

Examples

Molar mass of Na	$= 23\ g\ mol^{-1}$
Molar mass of ($C_{12}H_{22}O_{11}$)	$= 342\ g\ mol^{-1}$
Molar mass of $CaCl_2$	$= 111\ g\ mol^{-1}$
Molar mass of OH^{-1}	$= 17\ g\ mol^{-1}$

Molar Volume

"The volume occupied by one mole of an ideal gas at standard temperature and pressure (STP) i.e $0^{\circ}C$ and 1 atm is called molar volume."

Symbol Its symbol is V_m

Value Its value is 22.414 dm^3 (0.022414 m^3 or 22414 cm^3)

Examples

(i) 2g of H_2 = 1 mole of H_2 = 22.414 dm^3

(ii) 16g of CH_4 = 1 mole of CH_4 = 22.414 dm^3

From above examples it is clear that 1 mole of different gases have same number of molecules and same volume at STP but different masses.

Q9. (f) 2 g of H_2, 16 g of CH_4 and 44 g of CO_2 occupy separately the volumes of 22.414 dm^3, although the sizes and masses of three gases are very different from each other.

Ans. 2g of H_2 = 1 mol H_2 = 6.02×10^{23} molecule = 22.414 dm^3

16 g of CH_4 = 1 mol CH_4 = 6.02×10^{23} molecules = 22.414 dm^3

44 g of CO_2 = 1 mol CO_2 = 6.02×10^{23} molecules = 22.414 dm^3

According to Avogadro's law, equal moles of gases at same temperature and pressure (STP) occupy same volume. One mole of any gas can occupy 22.414 dm^3 at STP. So 2g of H_2, 16g of CH_4 and 44g of CO_2 occupy 22.414 dm^3.

Volume occupied by a gas does not depend on size and mass of gas molecule. It only depends on number of molecules. Reason is that at STP, distance between gas molecules is 300 times greater than their own diameters

Q23. (a) What is stoichiometry? Give its assumptions? Mention two important laws, which help to perform the stoichiometric calculations?

Stoichiometry

"The branch of chemistry which deals with the study of quantitative relationship between reactants and products in a balanced chemical equation is called stoichiometry."

Stoichiometric Amounts

"The amounts of the reactants or the products as given by the balanced chemical equation are called stoichiometric amounts."

$2H_2$	+	O_2	$\longrightarrow$	$2H_2O$
2 mole		1 mole		2 moles
4 g		32 g		36 g

Assumptions

When stoichiometric calculations are performed, we have to assume the following conditions

(i) All the reactants are completely converted into products.

(ii) No side reaction occurs.

During stoichiometric calculations, law of conservation of mass and law of definite proportions are obeyed.

Relationships

(i) Mass-mass relationship

If we are given mass of one substance, we can calculate the mass of the other substance involved in the chemical reaction.

(ii) Mass-mole relationship

If we are given mass of one substance, we can calculate the moles of the other substance and vice versa.

(iii) Mass-volume relationship

If we are given mass of one substance, we can calculate the volume of the other substance and vice versa.

Similarly, mole-mole calculations can also be performed.

Law of Conservation of mass:

- In all physical and chemical changes, the total mass of the reactants is equal to that of the products.
- It was studied by Antonie Lavoisier (1774).

The Law of Definite proportions or Constant composition:

- The law was given by J.L.Proust and deals with the composition of elements present in a compound.
- The law states that: The same compound always contain the same elements combined together in the same fixed proportion by weight.
- The composition of the compound is always the same irrespective of the method by which it is produced.

Chemical Equation

"A statement that describes a chemical reaction in terms of symbols and chemical formulas is called a chemical equation."

$$C + O_2 \longrightarrow CO_2$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Balancing a chemical equation

There are three methods to balance a chemical equation

(i) Hit and trial method

(ii) Redox method

(iii) Ion electron method

Limitations of a chemical equation

The demerits of a chemical equation are as follows

- A chemical equation does not tell the rate of the reaction.
- It does not tell the conditions, necessary for the reaction.
- It does not give colour, odour or state of the reactants and the products.
- We can even write the chemical equation of the reaction that does not occur.

Limiting Reactant

"A reactant which is used or consumed earlier due to its lesser amount and controls the amount of product formed in a chemical reaction is called limiting reactant."

A limiting reactant is that which

(i) controls the amount of product formed

(ii) is taken in lesser amount

(iii) is consumed earlier

(iv) produces least amount of product

Examples

(1) Consider the following reaction between H_2 and O_2 to form water

$2H_2$	+	O_2	$\longrightarrow$	$2H_2O$
2 mole		1 mole		2 moles

Suppose, we allow 2 moles of hydrogen (4g) to react with 2 moles of oxygen (64g). According to the above equation 2 moles of hydrogen (4g) will react with only one mole of oxygen (32g) to produce two moles of water (36g). Hence, one mole of oxygen (32g) will be left un-reacted because the whole of the given amount of H_2 has been consumed. Therefore, no more reaction will take place. In this case, H_2 is the limiting reactant because it is consumed first during the chemical reaction and controls the chemical reaction between hydrogen and oxygen.

(2) Consider the following reaction between carbon and oxygen to produce carbon dioxide

$$\underset{\textbf{1 mole}}{C} + \underset{\textbf{1 mole}}{O_2} \longrightarrow \underset{\textbf{1 moles}}{CO_2}$$

Suppose, we allow 2 moles of carbon to react with one mole of oxygen. According to the above equation one mole of oxygen will react with only one mole of carbon to form one mole of carbon dioxide. Hence, one mole of carbon will be left un-reacted because the whole of the amount of oxygen has been consumed. Therefore, no more reaction will take place. In this case oxygen will be the limiting reactant because it is consumed first during the chemical reaction and controls the chemical reaction between carbon and oxygen.

(3) Consider the following reaction between hydrogen and chlorine to form hydrochloric acid

$$\underset{\textbf{1 mole}}{H_2} + \underset{\textbf{1 mole}}{Cl_2} \longrightarrow \underset{\textbf{2 moles}}{2HCl}$$

Suppose, we allow one mole of hydrogen to react with 2 moles of chlorine. According to the above equation one mole of hydrogen will react with only one mole of chlorine to form two moles of hydrochloric acid. Hence, one mole of chlorine will be left un-reacted because the whole of the given amount of hydrogen has been consumed. Therefore, no more reaction will take place. In this case hydrogen will be the limiting reactant because it is consumed first during the chemical reaction and it is controlling the chemical reaction.

Identification of Limiting Reactant

Q. Write down steps involve in the determination of limiting reactant.

The following three steps should be followed to find out the limiting reactant

(i) Calculate the number of moles from the given amount of reactant

(ii) Find out the number of moles of product with the help of a balanced chemical equation

(iii) Identify the reactant which produces the least amount of product as limiting reactant

Q23b What is a limiting reactant? How does it control the quantity of the product formed? Explain with three examples.

Ans. Limiting reactant

"A limiting reactant is that reactant which controls the amount of product as it consumes earlier due to its smaller amount."

Examples

(i) If 2 moles H_2 and 2 moles O_2 are allowed to react then only 2 moles H_2O is produced

$2H_2 + O_2 \longrightarrow 2H_2O$

Here H_2 consumes completely and one mole O_2 left behind unreacted so H_2 is limiting reactant and limits the amount of H_2O upto 2 moles

(ii) During burning O_2 is in excess and a combustible material (coal, paper, candle etc.) is in smaller quantity. Combustible material is fully consumed and controls the amount of product so coal, candle or paper is limiting reactant.

(iv) If we have 20 slices and 9 kababs, we can only make 9 sandwiches as kababs are limiting reactant

Q. Concept of limiting reactant is not applicable on reversible reactions. Justify

Ans. "A reactant which consumes earlier due to its smaller amount and produces least amount of product is called limiting reactant."

During a reversible reaction, reactants are converted into products and products convert back into reactants. So reactants are not completely consumed. As a result a limiting reactant cannot be identified in a reversible reaction.

Yield

"The amount of products obtained in a chemical reaction is called yield."

Types

Yield is of three types

(i) Theoretical yield

"The amount of the products calculated from a balanced chemical equation is called theoretical yield."

- It is also known as calculated yield or expected yield.
- It is the maximum amount of the product which can be produced by a given amount of the reactant according to a balanced chemical equation.
- Theoretical yield of a reaction is always greater than the actual yield of the same reaction.

(ii) Actual yield

"The amount of the products obtained with a given amount of the reactant in an actual experiment is called actual yield."

- It is also known as experimental yield.
- The actual yield of a chemical reaction is always lesser than the theoretical yield.

(iii) Percentage yield

"It is equal to the ratio of the actual yield to the theoretical yield multiplied by 100."

Formula $$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

The efficiency of a chemical reaction is determined with the help of percentage yield.

Differentiate between Theoretical and Actual Yield

Theoretical Yield	Actual Yield
1) The amount of product calculated from a balanced chemical equation is called **theoretical yield**.	1) The amount of product obtained while performing a chemical reaction is called **actual yield**.
2) It is also called expected yield or calculated yield.	2) It is also called experimental yield.
3) Theoretical yield is always greater than actual yield.	3) Actual yield is always lesser than theoretical yield.
4) No need to perform experiment. Just to calculate from balanced chemical equation.	4) In order to get actual yield experiment has to be performed

Q 24. (a) How do we calculate the percentage yield of a chemical reaction.

Ans. We can calculate the percentage yield of a chemical reaction with the help of actual yield and theoretical yield of the reaction. The efficiency of a reaction is also expressed in the form of percentage yield

$$\text{Percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

Greater the percentage yield, more amount of reactants will convert into product and high will be the efficiency of reaction

KEY POINTS

1) Atoms are the building blocks of matter. Atoms can combine to form molecules. Covalent compounds mostly exist in the form of molecules. Atoms and molecules can either gain or lose electrons, forming charged particles called ions. Metals tend to lose electrons, becoming positively charged ions. Non-metals tend to gain electrons forming negatively charged ions. When X-rays or α – particles are passed through molecules in gaseous state, they are converted into molecular ions.

2) The atomic mass of an element is determined with reference to the mass of carbon as a standard element and is expressed in amu. The fractional atomic masses can be calculated form the relative abundance of isotopes. The separation and identification of isotopes can be carried out by mass spectrograph

3) The composition of a substance is given by its chemical formula. A molecular substance can be represented by its empirical or molecular formulas. The empirical and molecular formulas are related through a simple integer

4) Combustion analysis is one of the techniques to determine the empirical formula and then the molecular formula of a substance by knowing its molar mass.

5) A mole of any substance is the Avogdro's number of atoms or molecules or formula units of that substance.

6) The study of quantitative relationship between the reactants and the products in a balanced equation is known as stoichiometry The mole concept can be used to calculate the relative quantities of reactants and products in a balanced chemical equation.

7) The concept of molar volume of gases helps to relate solids and liquids with gases in a quantitate manner.

8) A limiting reactant is completely consumed in a reaction and controls the quantity of products formed.

9) The theoretical yield of a reaction is the quantity of the products calculated with the help of a balanced chemical equation The actual yield of a reaction is always less than the theoretical yield. The efficiency of a chemical reaction can be checked by calculating its percentage yield

SOLVED OBJECTIVE EXERCISE

Q1. Select the most suitable answer from the given ones in each questions

(i) Isotopes differ in
- (a) properties depend upon mass
- (b) arrangement of electron in orbitals
- (c) chemical properties
- (d) the extent to which they may be affected in electromagnetic field

(ii) Which of the following statement is not true
- (a) isotopes with even atomic masses are comparatively abundant
- (b) isotopes with odd atomic masses are comparatively less abundant
- (c) isotopes with even atomic masses and even atomic numbers are comparatively abundant
- (d) isotopes with even atomic masses and odd atomic numbers are comparatively abundant

(iii) Many elements have fractional atomic masses. This is because
- (a) the mass of atom is itself fractional
- (b) atomic masses are average masses of isobars
- (c) atomic masses are average masses of isotopes
- (d) atomic masses are average masses of isotopes proportional to their relative abundance

(iv) The mass of one mole of electron is
- (a) 1.008 mg
- (b) 0.55 mg
- (c) 0.184 mg
- (d) 1.637 mg

(v) 27 g of Al will react completely with how much mass of O_2 to produce Al_2O_3
- (a) 8 g of oxygen
- (b) 16 g of oxygen
- (c) 32 g of oxygen
- (d) 24 g of oxygen

(vi) The number of moles of CO_2 which contain 8.0 g of oxygen
- (a) 0.25
- (b) 0.50
- (c) 1.0
- (d) 1.5

(vii) The largest number of molecules are present in
- (a) 3.6 g of H_2O
- (b) 4.8 g of C_2H_5OH
- (c) 2.8 g of CO
- (d) 5.4 g of N_2O_5

(viii) One mole of SO_2 contains
- (a) 6.02×10^{23} of oxygen atoms
- (b) 18.1×10^{23} molecules of SO_2
- (c) 6.02×10^{23} of sulphur atoms
- (d) 4 gram atoms of SO_2

(ix) The volume occupied by 1.4 g of N_2 at STP is
- (a) 2.24 dm^3
- (b) 22.4 dm^3

- (c) 1.12 dm^3
- (d) 112 cm^3

(x) A limiting reactant is the one which
- (a) is taken in lesser quantity in grams as compared to the other reactants
- (b) is taken in lesser quantity in volume as compared to the other reactants
- (c) gives the maximum amount of the product which is required
- (d) gives the minimum amount of product under consideration

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	**(a) properties depend upon mass**	Isotopes are sister atoms of same element which differ by their atomic masses due to different number of neutrons They show different deflection in magnetic field due to their different m/e values
(ii)	**(c) isotopes with even atomic masses and even atomic numbers are comparatively abundant**	The elements of even atomic number usually have larger number of isotopes. The isotopes whose mass numbers are multiple of four are particularly abundant. For example ^{16}O, ^{24}Mg, ^{28}Si, ^{40}Ca and ^{56}Fe. These isotopes exist abundantly and form about **50%** of the earth crust. Out of **280** isotopes that occur in nature, **154** isotopes have even atomic number and even mass number
(iii)	**(d) atomic masses are average masses of isotopes proportional to their relative abundance**	The atomic mass of an element is calculated from i) Isotopic masses ii) Relative abundance
(iv)	**(b) 0.55 mg**	1 mole of electron = 6.022×10^{23} Mass of one electron = 9.1095×10^{-31} kg Mass of 1 mole of electron = $6.022 \times 10^{23} \times 9.1095 \times 10^{-31}$ $= 54.85 \times 10^{-8}$ kg $= 54.85 \times 10^{-8} \times 10^{6}$ kg $= 54.85 \times 10^{-2}$ mg $= 0.55$ mg
(v)	**(d) 24 g of oxygen**	$4Al + 3O_2 \longrightarrow 2Al_2O_3$ Mol of Al $= \frac{27}{27} = 1$ mol Al : O_2 4 ml 3 mol 1 mol : $\frac{3}{4} = 0.75$ mol Mass of $O_2 = 0.75 \times 32 = 24$g of oxygen
(vi)	**(a) 0.25**	C O_2 ↓ ↓ 12g 32g = 44g = 1mol ↓ 16g = 22g = 0.50mol ↓ 8g = 11g = 0.25mol
(vii)	**(a) 3.6 g of H_2O**	Greater the number of moles of a substance greater will be its number of

3

		molecules. (a) $\frac{3.6}{18} = 0.2mol$ (b) $\frac{4.8}{48} = 0.1mol$ (c) $\frac{2.8}{28} = 0.1mol$ (d) $\frac{5.4}{108} = 0.05mol$
(viii)	(c) 6.02×10^{23} of sulphur atoms	1 mole of $SO_2 = 6.022 \times 10^{23}$ SO_2 molecules 1 molecule of SO_2 contains one sulphur atom. So 6.022×10^{23} SO_2 molecules contain 6.022×10^{23} S – atoms
(ix)	(c) 1.12 dm^3	Molecular mass of $N_2 = 28gmol^{-1}$ 28g of N_2 at STP occupies volume = 22.414 dm^3 14g of N_2 at STP occupies volume = 11.207 dm^3 1.4g of N_2 at STP occupies volume = 1.12 dm^3
(x)	(d) gives the minimum amount of product under consideration	A reactant which is used or consumed earlier due to its lesser amount and controls the amount of product formed in a chemical reaction is called limiting reactant

Q2. Fill in the blanks

(i) The unit of relative atomic mass is ________

(ii) The exact masses of isotopes can be determined by ________ spectrograph.

(iii) The phenomenon of isotopy was first discovered by ________

(iv) The empirical formula can be determined by combustion analysis for those compounds which have ________ and ________ in them

(v) A limiting reactant is that which controls the quantities of ________

(vi) 1 mole of glucose has ________ atoms of carbon, ________ atoms of oxygen and ________ atoms of hydrogen.

(vii) 4 g of CH_4 at 0°C and 1 atm pressure has ________ molecules of CH_4

(viii) Stoichiometric calculations can be performed only when ________ is obeyed.

ANSWERS

(i) atomic mass unit (a.m.u)	(ii) Aston's mass
(iii) Soddy	(iv) Carbon, hydrogen
(v) product	(vi) 3.612×10^{24}, 3.612×10^{24}, 7.224×10^{24}
(vii) 1.505×10^{23}	(viii) law of conservation of mass and law of definite proportion

Q3. Indicate 'True' or 'False'

(i) Ne has three isotopes and fourth one with atomic mass of 20.18 a.m.u.

(ii) Empirical formula gives us the information about the total number of atoms present in the molecule

(iii) During combustion analysis $Mg(ClO_4)_2$ is employed to absorb water vapours.

(iv) Molecular formula is the integral multiple of empirical formula and the integral multiple can never be unity.

(v) The number of atoms in 1.79 g of gold and 0.023 g of sodium are equal.

(vi) The number of electrons in the molecules of CO and N_2 are 14 each, so 1 mg of each gas will have same number of electrons

(vii) Avogadro's hypothesis is applicable to all types of gases i.e., ideal and non-ideal.

(viii) Actual yield of a chemical reaction may be greater than the theoretical yield.

ANSWERS

(i) False	(ii) False	(iii) True	(iv) False
(v) False	(vi) True	(vii) False	(viii) False

SHORT ANSWERS TO EXERCISE

Q24. (b)What are the factors which are mostly responsible for the low yield of the products in chemical reactions?
Or Why actual yield is always less than theoretical yield.

Ans. Actual yield of a chemical reaction is usually lesser than theoretical yield due to many reasons. They are.

(i) **Practically inexperienced** worker has many shortcomings and cannot get expected yield

(ii) **Mechanical loss** during experimentation e.g., filtration, separation by distillation or by a separating funnel, washing, drying and crystallization if not properly carried out, decrease the yield.

(iii) Some of the reactants might take part in a **competing side reaction.**

(iv) The reaction might be **reversible**

(v) The reactants might be **impure**

(vi) Sometimes the **reaction conditions** are not suitably maintained.

Q25. Explain the following with reasons.

(i) Law of conservation of mass has to be obeyed during stoichiometric calculations.

Ans. According to law of conservation of mass
"Mass can neither be created nor destroyed during a chemical reaction but it changes its form from one form to another"
In stoichiometric calculations we use balanced chemical equation where total mass of reactants is equal to the total mass of products

For example

- $2H_2 + O_2 \longrightarrow 2H_2O$
  $4g + 32g \longrightarrow 36g$
- $NaOH + HCl \longrightarrow NaCl + H_2O$
  $40g + 36.5g \longrightarrow 58.5g + 18g$
  $76.5g \longrightarrow 76.5g$

So while doing stoichiometric calculations law of conservation of mass has to be obeyed

(ii) Many chemical reactions taking place in our surrounding involve the limiting reactants.

Ans. "The reactant which is consumed earlier and controls the amount of product in a chemical reaction is called a limiting reactant."
Mostly combustion reactions taking place in our surroundings involve the limiting reactant

For example

- $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$
- $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

In above examples O_2 gas is present in excess while CH_4 and C are the reactants which consume earlier so they are limiting reactants

(iii) No individual neon atom in the sample of the element has a mass of 20.18 amu.

Ans. 20.18 amu is the average atomic mass of neon which is obtained by using different isotopic masses and relative abundances of Neon as follows.

Neon has three isotopes ^{20}Ne, ^{21}Ne and ^{22}Ne with a relative abundance of 90.92%, 0.26% and 8.82% respectively.

$$\text{Average atomic mass of neon} = \frac{\text{Sum of product of isotopic masses and relative abundances}}{100}$$

		molecules (a) $\frac{3.6}{18} = 0.2mol$ (b) $\frac{4.8}{48} = 0.1mol$ (c) $\frac{2.8}{28} = 0.1mol$ (d) $\frac{5.4}{108} = 0.05mol$
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(ix)	**(c) 1.12 dm^3**	Molecular mass of $N_2 = 28gmol^{-1}$ 28g of N_2 at STP occupies volume = 22.414 dm^3 14g of N_2 at STP occupies volume = 11.207 dm^3 1.4g of N_2 at STP occupies volume = 1.12 dm^3
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$$\text{Average atomic mass of neon} = \frac{\text{Sum of product of isotopic masses and relative abundaces}}{100}$$

$$= \frac{(90.92 \times 20) + (0.26 \times 21) + (8.82 \times 22)}{100}$$

$= 20.18$ amu

So no individual Ne atom has a mass of 20.18 amu.

(iv) One mole of H_2SO_4 should completely react with two moles of NaOH. How does Avogadro's number help to explain it?

Ans. "A process in which one mole of water is produced by its ionic components i.e., H^+ and OH^- coming from acid and base respectively is called neutralization."

$$H^+ + OH^- \rightleftharpoons H_2O$$

H_2SO_4 being a dibasic acid can produce 2 mole H^+ ions on ionization in water

$$H_2SO_{4(aq)} \rightleftharpoons 2H^+_{(aq)} + SO^{2-}_{4(aq)}$$

On the other hand NaOH being monoacid produces only one mole OH^- in aqueous solution

$$NaOH_{(aq)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$

To neutralize 2 moles H^+ ions of H_2SO_4, we need 2 moles of OH^- so

$$2H^+ + 2OH^- \rightleftharpoons 2H_2O$$

2 moles of H^+ $= 2 \times 6.02 \times 10^{23}$ ions $= 12.04 \times 10^{23}$ ions

2 moles of OH^- $= 2 \times 6.02 \times 10^{23}$ ions $= 12.04 \times 10^{23}$ ions

so

12.04×10^{23} H^+ ions + 12.04×10^{23} OH^- ions are used to produce 12.04×10^{23} H_2O molecules.

Hence one mole of H_2SO_4 is neutralized by 2 moles of NaOH.

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

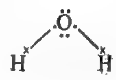
(v) One mole of H_2O has two moles of bonds, three moles of atoms, ten moles of electrons and twenty eight moles of total fundamental particles in it.

Ans. Water molecule is formed when two atoms of hydrogen combine with one atom of oxygen.

${}^{16}_{8}O = 8e + 8p + 8n$

${}^{1}_{1}H = 1e + 1p + 0n$

${}^{1}_{1}H = 1e + 1p + 0n$



Total sub atomic particles of H_2O = 10e + 10p + 8n = 28 particles

As shown by the formula of one molecule of water

(i) 1 molecule of H_2O contains bonds = 2

1 mol H_2O molecules contains bonds = 2 moles

(ii) 1 molecule of H_2O contains atoms = 3

1 mole H_2O molecules contain atoms = 3 moles

(iii) 1 H_2O molecule contains electrons = 8 + 1 + 1 = 10

1 mol H_2O molecule contain electrons = 10 moles

(iv) 1 H_2O molecule has subatomic particles = 28

1 mol H_2O molecule have subatomic particles = 28 moles

(vi) N_2 and CO have the same number of electrons, protons and neutrons.

Ans.

N_2	CO
${}^{14}_{7}N = 7e + 7p + 7n$ One molecule of nitrogen contains two nitrogen atoms	${}^{12}_{6}C = 6e + 6p + 6n$ ${}^{16}_{8}O = 8e + 8p + 8n$ One molecule of carbon monoxide contains one carbon and one oxygen atom

so N = 7e + 7p + 7n + N = 7e + 7p + 7n Total N_2 = 14e + 14p + 14n	so C = 6e + 6p + 6n + O = 8e + 8p + 8n Total CO = 14e + 14p + 14n

So N_2 and CO have same number of electrons, protons and neutrons

NUMERICALS OF EXERCISE

Q10. Calculate each of the following quantities.

(a) Mass in grams of 2.74 moles of $KMnO_4$.

Ans. Given data

Number of moles of $KMnO_4$ = 2.74 moles

Required

Mass in grams of $KMnO_4$ = ?

Solution

$$\text{Number of moles of } KMnO_4 = \frac{\text{Mass of } KMnO_4}{\text{Formula mass of } KMnO_4}$$

Formula mass of $KMnO_4$ $= 39 + 55 + 64 = 158 \text{ g mol}^{-1}$

$$2.74 = \frac{\text{Mass of } KMnO_4}{158}$$

158×2.74 = Mass of $KMnO_4$

432.92 g = Mass of $KMnO_4$

(b) Moles of O atoms in 9.00 g of $Mg(NO_3)_2$.

Ans. Given data

Mass of $Mg(NO_3)_2$ = 9.00 g

Required

Number of moles of O atoms = ?

Solution

$$\text{Number of moles of } Mg(NO_3)_2 = \frac{\text{Mass of } Mg(NO_3)_2}{\text{Molar mass of } Mg(NO_3)_2}$$

Molar Mass of $Mg(NO_3)_2$ $= 24 + 2(14 + 3 \times 16) = 148 \text{ g mol}^{-1}$

$$\text{Number of moles of } Mg(NO_3)_2 = \frac{9}{148} = 0.06 \text{ moles}$$

1 mole of $Mg(NO_3)_2$ contains O atoms = 6 moles

0.06 moles of $Mg(NO_3)_2$ contain moles of O atoms $= 0.06 \times 6 = 0.36$ atoms

(c) Number of O atoms in 10.037 g of $CuSO_4.5H_2O$

Ans. Given data

Mass of $CuSO_4.5H_2O$ = 10.037 g

Required

Number of O atoms = ?

Solution

$$\text{Number of moles of } CuSO_4.5H_2O = \frac{\text{Mass of } CuSO_4.5H_2O}{\text{Molar mass of } CuSO_4.5H_2O}$$

Molar Mass of $CuSO_4.5H_2O$ $= 63.5 + 32 + (4 \times 16) + (5 \times 18) = 249.5\ g\ mol^{-1}$

Number of moles of $CuSO_4.5H_2O$ $= \dfrac{10.037}{249.5}$

$= 0.04$ moles

1 moles of $CuSO_4.5H_2O$ have moles of O $= 9$ moles

0.04 moles of $CuSO_4.5H_2O$ have moles of O $= 9 \times 0.04$

$= 0.36$ moles

Number of Oxygen atoms = Number of moles of oxygen atoms $\times N_A$

$= 0.36 \times 6.02 \times 10^{23}$

Number of Oxygen atoms $= 2.167 \times 10^{23}$ **atoms**

(d) Mass in kilograms of 2.6×10^{20} molecules of SO_2.

Ans. Given data

Number of SO_2 molecules $= 2.6 \times 10^{20}$ molecules

Required

Mass in kg of SO_2 molecules $= ?$

Solution

Number of SO_2 molecules $= \dfrac{\text{Mass of } SO_2 \text{ molecules}}{\text{Molar mass of } SO_2} \times N_A$

Molar Mass of SO_2 $= 32 + (16 \times 2) = 64\ g\ mol^{-1}$

$2.6 \times 10^{20} = \dfrac{\text{Mass of } SO_2 \text{ molecules}}{64} \times 6.02 \times 10^{23}$

$\dfrac{2.6 \times 10^{20} \times 64}{6.02 \times 10^{23}}$ = Mass of SO_2 molecules

$27.641 \times 10^{-3}\ g =$

$\dfrac{27.641 \times 10^{-3}}{1000} =$

$2.764 \times 10^{-5}\ kg$ = Mass of SO_2 molecules

(e) Moles of Cl atoms in 0.822 g $C_2H_4Cl_2$.

Ans. Given data

Mass of $C_2H_4Cl_2 = 0.822$ g

Required

Number of moles of Cl atoms $= ?$

Solution

Number of moles of $C_2H_4Cl_2$ $= \dfrac{\text{Mass of } C_2H_4Cl_2}{\text{Molar mass of } C_2H_4Cl_2}$

Molar Mass of $C_2H_4Cl_2$ $= 24 + 4 + 71 = 99\ g\ mol^{-1}$

Number of moles of $C_2H_4Cl_2$ $= \dfrac{0.822}{99}$

$= 0.0083$ moles

1 mole of $C_2H_4Cl_2$ contains moles of Cl atoms $= 2$ moles

0.0083 moles of $C_2H_4Cl_2$ contain moles of Cl atoms $= 0.0083 \times 2 = 0.0166$ **moles**

(f) Mass in grams of 5.136 moles of Ag_2CO_3.

Ans. Given data

Moles of Ag_2CO_3 $= 5.136$ moles

Required

Mass of Ag_2CO_3 $= ?$

Solution

Number of moles of Ag_2CO_3 $= \dfrac{\text{Mass of } Ag_2CO_3}{\text{Formula Mass of } Ag_2CO_3}$

Formula mass of Ag_2CO_3 $= (108 \times 2) + 12 + (16 \times 3) = 276\ g\ mol^{-1}$

$5.136 = \dfrac{\text{Mass of } Ag_2CO_3}{276}$

5.136×276 = Mass of Ag_2CO_3

1417.54 g = Mass of Ag_2CO_3

(g) Mass in grams of 2.78×10^{21} molecules of CrO_2Cl_2.

Ans. Given data

Number of molecules of $CrO_2Cl_2 = 2.78 \times 10^{21}$ molecules

Required

Mass of molecules of CrO_2Cl_2 in gram $= ?$

Solution

Number of molecules of CrO_2Cl_2 $= \dfrac{\text{Mass of } CrO_2Cl_2}{\text{Molar mass of } CrO_2Cl_2} \times N_A$

Molar Mass of CrO_2Cl_2 $= 52 + 32 + 71 = 155\ g\ mol^{-1}$

$2.78 \times 10^{21} = \dfrac{\text{Mass of } CrO_2Cl_2}{155} \times 6.02 \times 10^{23}$

$\dfrac{2.78 \times 10^{21} \times 155}{6.02 \times 10^{23}}$ = Mass of CrO_2Cl_2

0.7158 g = Mass of CrO_2Cl_2

(h) Number of moles and formula units in 100 g of $KClO_3$.

Ans. Given data

Mass of $KClO_3$ $= 100$ g

Required

Number of moles of $KClO_3$ $= ?$

Number of formula units of $KClO_3$ $= ?$

Solution

Number of moles of $KClO_3$ $= \dfrac{\text{Mass of } KClO_3}{\text{Molar mass of } KClO_3}$

Molar Mass of $KClO_3$ $= 39 + 35.5 + 48 = 122.5\ g\ mol^{-1}$

Number of moles of $KClO_3$ $= \dfrac{100}{122.5} = 0.816$ **moles**

1 mole of $KClO_3$ contains formula units $= 6.02 \times 10^{23}$

0.816 moles of $KClO_3$ contain formula units $= 0.816 \times 6.02 \times 10^{23}$

$= 4.91 \times 10^{23}$ formula units

(i) Number of K^+ ions, ClO_3^{-1} ions, Cl atoms, and O atoms in 100g of $KClO_3$ (h).

Ans. 1 mole of $KClO_3$ contains K^+ ions $= 6.02 \times 10^{23}$

0.816 moles of $KClO_3$ contain K^+ ions $= 0.816 \times 6.02 \times 10^{23}$

$= \mathbf{4.91 \times 10^{23}}$ **ions**

1 mole of $KClO_3$ contains ClO_3^- ions $= 6.02 \times 10^{23}$

0.816 moles of $KClO_3$ contain ClO_3^- ions $= 0.816 \times 6.02 \times 10^{23} = \mathbf{4.91 \times 10^{23}}$ **ions**

Similarly,

1 mole of $KClO_3$ contains Cl atoms $= 6.02 \times 10^{23}$

0.816 mol of $KClO_3$ contain Cl atoms $= \mathbf{4.91 \times 10^{23}}$ **atoms**

1 mole of $KClO_3$ contains O atoms $= 3 \times 6.02 \times 10^{23}$ atoms

0.816 moles of $KClO_3$ contain O atoms $= 0.816 \times 3 \times 6.02 \times 10^{23}$

$= \mathbf{1.474 \times 10^{24}}$ **atoms**

Q11. Aspartame, the artificial sweetener, has a molecular formula of $C_{14}H_{18}N_2O_5$.

(a) What is the mass of one mole of aspartame?

Ans. 1 mole of $C_{14}H_{18}N_2O_5$ $= (12\times14) + (1\times18) + (14\times2) + (16\times5)$

$= 168 + 18 + 28 + 80$

$= \mathbf{294\ g\ mol^{-1}}$

(b) How many moles are present in 52 g of aspartame?

Ans. Given data

Mass of aspartame $= 52$ g

Required

Number of moles of aspartame $= ?$

Solution

$$\text{Number of moles of aspartame} = \frac{\text{Mass of aspartame}}{\text{Molar mass of aspartame}}$$

Molar mass of $C_{14}H_{18}N_2O_5$ $= (12 \times 14) + 18 + 28 + (16 \times 5) = 294\ g\ mol^{-1}$

$$\text{Number of moles of aspartame} = \frac{52}{294} = 0.177 \text{ moles}$$

(c) What is the mass in grams of 10.122 moles of aspartame?

Ans. Given data

moles of Aspartame $= 10.122$ moles

Required

Mass of aspartame $= ?$

Solution

$$\text{Number of moles of aspartame} = \frac{\text{Mass of aspartame}}{\text{Molar mass of aspartame}}$$

Molar mass of $C_{14}H_{18}N_2O_5$ $= (12 \times 14) + 18 + 28 + (16 \times 5) = 294\ g\ mol^{-1}$

$$10.122 = \frac{\text{Mass of aspartame}}{294}$$

10.122×294 = Mass of aspartame

2975.87 g = Mass of aspartame

(d) How many hydrogen atoms are present in 2.43 g of aspartame?

Ans. Given data

Molecular formula of Aspartame $= C_{14}H_{18}N_2O_5$

Mass of Aspartame $= 2.43$ g

Required

Number of hydrogen atoms $= ?$

Solution

$$\text{Number of moles of aspertame} = \frac{\text{Mass of aspartame}}{\text{Molar mass of aspartame}}$$

Molar mass of $C_{14}H_{18}N_2O_5$ $= (12\times14) + (1\times18) + (2\times14) + (16\times5)$

$= 168 + 18 + 80 + 28$

$= 294\ g\ mol^{-1}$

$$= \frac{2.43}{294} = 0.00826 \text{ moles}$$

Moles of hydrogen in one mole of aspartame $= 18$ moles

0.00826 moles of aspartame have moles of hydrogen $= 0.0826 \times 18 = 0.1487$

Number of atoms of hydrogen = Number of moles of aspartame $\times N_A$

$= 0.1487 \times 6.02 \times 10^{23}$

$= 0.8951 \times 10^{23}$

Number of atoms of hydrogen $= \mathbf{8.96 \times 10^{22}}$ **atoms**

Q12. A sample of 0.600 moles of a metal M reacts completely with excess of fluorine to form 46.8 g of MF_2.

(a) How many moles of F are present in the sample of MF_2 that forms?

(b) Which element is represented by the symbol M?

Ans. Given data

Number of moles of M $= 0.600$ moles

Mass of MF_2 $= 46.8$ g

Required

Number of moles of F $= ?$

Actual name of Metal M $= ?$

Solution

$$M + F_2 \longrightarrow MF_2$$

Comparison between number of moles of M and MF_2

M	:	MF_2
1	:	1
0.6	:	0.6

Number of moles of MF_2 $= \mathbf{0.6\ moles}$

1 mole of MF_2 contain moles of F atoms = 2

0.6 moles of MF_2 contain moles of F atoms $= 0.6 \times 2 = \mathbf{1.2\ moles}$

Number of moles of MF_2 $= \dfrac{\text{Mass of } MF_2}{\text{Molar mass of } MF_2}$

0.6 mol $= \dfrac{46.8\,g}{\text{Molar mass of } MF_2}$

Molar mass of MF_2 $= \dfrac{46.8\,g}{1.2\,mol} = 78\,g\,mol^{-1}$

Atomic mass of M + (19 × 2) $= 78\,g\,mol^{-1}$ **(Atomic Mass of F = 19)**

$M + 38 = 78$

$M = 78 - 38$

Atomic mass of M $= 40\ g\,mol^{-1}$

So, Actual name of Metal M = Calcium (Ca)

Q13. In each pair, choose the larger of the indicated quantity, or state if the samples are equal.

(a) Individual particles 0.4 moles of oxygen molecules or 0.4 moles of oxygen atoms.

Ans. **Both are equal.**

Reason

0.4 moles of O_2 molecules and 0.4 moles of O atoms, both are equimolar quantities so, they have equal number of particles. i.e.

$0.4 \times 6.02 \times 10^{23} = 2.408 \times 10^{23}$ moles

(d) Individual particles 4.0 g of N_2O_4 or 3.3 g of SO_2.

Given data

Mass of N_2O_4 = 4 g

Mass of SO_2 = 3.3 g

Required

Individual particles N_2O_4 = ?

Individual particles SO_2 = ?

Solution

(i) Number of molecules of N_2O_4 $= \dfrac{\text{Mass of } N_2O_4}{\text{Molar mass of } N_2O_4} \times N_A$

Molar Mass of N_2O_4 $= (14 \times 2) + (16 \times 4) = 92\ g\,mol^{-1}$

$= \dfrac{4}{92} \times 6.02 \times 10^{23}$

$= 0.258 \times 10^{23}$

Number of molecules of N_2O_4 $= \mathbf{2.58 \times 10^{22}}$ **molecules**

(ii) Number of molecules of SO_2 $= \dfrac{\text{Mass of } SO_2}{\text{Molar mass of } SO_2} \times N_A$

Molar Mass of SO_2 $= 32 + 32 = 64\ g\,mol^{-1}$

$= \dfrac{3.3}{64} \times 6.02 \times 10^{23}$

$= 0.3104 \times 10^{23}$

Number of molecules of SO_2 $= \mathbf{3.1 \times 10^{22}}$ **molecules**

3.3 g of SO_2 has larger number of individual particles.

(e) Total ions 2.3 moles of $NaClO_3$ or 2.0 moles o $MgCl_2$?

Ans. **Given data**

Number of moles of $NaClO_3$ = 2.3 moles

Number of moles of $MgCl_2$ = 2 moles

Required

Number of ions in 2.3 moles of $NaClO_3$ = ?

Number of ions in 2 moles of $MgCl_2$ = ?

Solution

(i) 1 mole of $NaClO_3$ contains Na^+ ions $= 6.02 \times 10^{23}$

2.3 moles of $NaClO_3$ contain Na^+ ions $= 2.3 \times 6.02 \times 10^{23}$

$= 13.846 \times 10^{23}$ ions

1 mole of $NaClO_3$ contains ClO_3^- ions $= 6.02 \times 10^{23}$

2.3 moles of $NaClO_3$ contain ClO_3^- ions $= 2.3 \times 6.02 \times 10^{23}$

$= 13.846 \times 10^{23}$ ions

Total ions of $NaClO_3$ $= Na^+$ ions + ClO_3^- ions

$= 13.846 \times 10^{23} + 13.846 \times 10^{23}$

Total ions of $NaClO_3$ $= \mathbf{2.7692 \times 10^{24}}$ **ions**

(ii) 1 mole of $MgCl_2$ contain Mg^{2+} ions $= 6.02 \times 10^{23}$

2 mole of $MgCl_2$ contain Mg^{2+} ions $= 2 \times 6.02 \times 10^{23}$

$= 12.04 \times 10^{23}$ ions

1 mole of $MgCl_2$ contain Cl^- ions $= 2 \times 6.02 \times 10^{23}$

2 moles of $MgCl_2$ contain Cl^- ions $= 2 \times 2 \times 6.02 \times 10^{23}$

$= 24.04 \times 10^{23}$

Total ions of $MgCl_2$ $= Mg^{2+}$ ions + Cl^- ions

$= 12.04 \times 10^{23} + 24.04 \times 10^{23}$

Total ions of $MgCl_2$ $= \mathbf{3.612 \times 10^{24}}$ **ions**

2 moles of $MgCl_2$ contain larger number of ions.

(f) Molecules 11.0 g H_2O or 11.0 g H_2O_2.

Ans. **Given data**

Mass of H_2O = 11.0 g

Mass of H_2O_2 = 11.0 g

Required

Number of molecules in 11 g of H_2O = ?

Number of molecules in 11g of H_2O_2 = ?

Solution

(i) Number of molecules of H_2O $= \dfrac{\text{Mass of } H_2O}{\text{Molar mass of } H_2O} \times N_A$

Molar Mass of H_2O $= 2 + 16 = 18\ g\,mol^{-1}$

Number of molecules of H_2O $= \dfrac{11}{18} \times 6.02 \times 10^{23}$

Number of molecules $= \mathbf{3.67 \times 10^{23}}$ **molecules**

(ii) Number of molecules of H_2O_2 $= \dfrac{\text{Mass of } H_2O_2}{\text{Molar mass of } H_2O_2} \times N_A$

Molar Mass of H_2O_2 $= 2 + 32 = 34\ g\,mol^{-1}$

Number of moles of H_2O_2 $= \dfrac{11}{34} \times 6.02 \times 10^{23}$

Number of molecules $= \mathbf{1.948 \times 10^{23}}$ **molecules**

11g of H_2O contain larger number of molecules.

(g) Na ion 0.500 moles of NaBr or 0.0145 kg of NaCl

Ans **Given data**

Moles of NaBr = 0.500 moles

Mass of NaCl = 0.0145 kg = 14.5 g

Required

(i) Na^+ ions in 0.500 moles of NaBr = ?

(ii) Na^+ ions in 0.0145 kg of NaCl = ?

Solution

Number of formula units of NaBr = Number of moles of NaBr × N_A

$= 0.5 \times 6.02 \times 10^{23}$

Number of formula units of NaBr $= 3.01 \times 10^{23}$ formula units

Since one NaBr contains one Na^+ and one Br^-, So

Number of Na^+ ions $= 1 \times 3.01 \times 10^{23}$ ions

Number of Na^+ ions $= \mathbf{3.01 \times 10^{23}}$ **ions**

(ii) Number of formula units of NaCl $= \dfrac{\text{Mass of NaCl}}{\text{Formula Mass of NaCl}} \times N_A$

Molar Mass of NaCl $= 23 + 35.5 = 58.5\ g\,mol^{-1}$

Number of formula units of NaCl $= \dfrac{14.5}{58.5} \times 6.02 \times 10^{23}$

Number of formula units of NaCl $= 1.49 \times 10^{23}$ formula units

Since one NaCl contains one Na^+ and one Cl^-, So

Number of Na^+ ions $= 1 \times 1.49 \times 10^{23}$ ions

Number of Na^+ ions $= \mathbf{1.49 \times 10^{23}}$ **ions**

Number of Na^+ ions in 0.5 moles of NaBr is larger.

(h) Mass 6.02×10^{23} atoms of ^{235}U or 6.02×10^{23} atoms of ^{238}U.

Ans. **Given data**

Number of atoms $= 6.02 \times 10^{23}$ atoms

Required

Mass of atoms = ?

Solution

Isotopic mass of ^{235}U = 235 (1 mole)

Therefore,

6.02×10^{23} atoms of U^{235} have mass = **235 g**

Similarly,

6.02×10^{23} atoms of ^{238}U have mass = **238 g**

6.02×10^{23} atoms of ^{238}U have larger mass.

Q14. **(a) Calculate the percentage of nitrogen in the four important fertilizers i.e., (i) NH_3 (ii) NH_2CONH_2 (urea) (iii) $(NH_4)_2SO_4$ (iv) NH_4NO_3.**

(i) NH_3

Percentage of nitrogen $= \dfrac{\text{Mass of nitrogen}}{\text{Formula mass of compound}} \times 100$

Molar mass of NH_3 $= 14 + (3 \times 1) = 14 + 3 = 17\ g\,mol^{-1}$

$= \dfrac{14}{17} \times 100 = \mathbf{82.35\%}$

(ii) NH_2CONH_2

Molar mass of NH_2CONH_2 $= 14 + 2 + 12 + 16 + 14 + 2 = 60\ g\,mol$

Percentage of nitrogen $= \dfrac{28}{60} \times 100 = \mathbf{46.67\%}$

(iii) $(NH_4)_2SO_4$

Molar mass of $(NH_4)_2SO_4$ $= (14 \times 2) + (1 \times 8) + 32 + (16 \times 4)$

$= 132\ g\,mol^{-1}$

Percentage of nitrogen $= \dfrac{28}{132} \times 100 = \mathbf{21.21\%}$

(iv) NH_4NO_3

Molar mass of NH_4NO_3 $= 14 + 4 + 14 + 48 = 80\ g\,mol^{-1}$

Percentage of nitrogen $= \dfrac{28}{80} \times 100 = \mathbf{35\%}$

(b) Calculate the percentage of Nitrogen and Phosphorus in each of the following

(i) $NH_4H_2PO_4$

Formula mass of $NH_4H_2PO_4$ $= 14 + 4 + 2 + 31 + 64 = 115\ g\,mol^{-1}$

Percentage of nitrogen $= \dfrac{14}{115} \times 100 = \mathbf{12.17\%}$

Percentage of phosphorus $= \dfrac{31}{115} \times 100 = \mathbf{26.96\%}$

(ii) $(NH_4)_2HPO_4$

Molar mass of $(NH_4)_2HPO_4$ $= (14 \times 2) + (1 \times 8) + 1 + 31 + 64$

$= 132\ g\,mol^{-1}$

Percentage of nitrogen $= \dfrac{28}{132} \times 100 = \mathbf{21.21\%}$

Percentage of phosphorus $= \dfrac{31}{132} \times 100 = \mathbf{23.48\%}$

(iii) $(NH_4)_3PO_4$

Molar mass of $(NH_4)_3PO_4$ $= (14 \times 3) + 12 + 31 + 64$

$= 149\ g\,mol^{-1}$

Percentage of nitrogen $= \dfrac{42}{149} \times 100 = \mathbf{28.19\%}$

Percentage of phosphorus $= \dfrac{31}{149} \times 100 = \mathbf{20.81\%}$

Q15. **Glucose $C_6H_{12}O_6$ is the most important nutrient in the cell for generating chemical potential energy. Calculate the mass % of each element in glucose and determine the number of C, H and O atoms in 10.5 g of the sample.**

Ans. **Given data**

Mass of Glucose = 10.5 g

Required

Percentage of C = ?

Percentage of H = ?

Percentage of O = ?

Number of carbon atoms = ?

Number of hydrogen atoms = ?

Number of oxygen atoms = ?

Solution

Molar mass of $C_6H_{12}O_6$ $= (6 \times 12) + (1 \times 12) + (16 \times 6)$
$= 72 + 12 + 96 = 180\ g\,mol^{-1}$

Percentage of an element $= \dfrac{\text{Mass of element}}{\text{Molar mass}} \times 100$

Percentage of carbon $= \dfrac{72}{180} \times 100 = 40\%$

Percentage of hydrogen $= \dfrac{12}{180} \times 100 = 6.66\%$

Percentage of oxygen $= \dfrac{96}{180} \times 100 = 53.33\%$

Number of molecules of Glucose $= \dfrac{\text{Mass}}{\text{Molar mass}} \times N_A$

$= \dfrac{10.5}{180} \times 6.02 \times 10^{23}$

Number of molecules of $C_6H_{12}O_6 = 0.351 \times 10^{23}$ molecules

1 molecule of glucose contain carbon atoms $= 6 \times 0.351 \times 10^{23}$
$= 2.107 \times 10^{23}$ atoms

1 molecule of glucose contain hydrogen atoms $= 12 \times 0.351 \times 10^{23}$
$= 4.212 \times 10^{23}$ atoms

1 molecule of glucose contain oxygen atoms $= 6 \times 0.351 \times 10^{23}$
$= 2.107 \times 10^{23}$ atoms

Q16. Ethylene glycol is used as automobile antifreeze. It has 38.7% carbon, 9.7% hydrogen and 51.6% oxygen. Its molar mass is 62.1 grams mol^{-1}. Determine its empirical formula.

Ans. Given data

Percentage of carbon $= 38.7\%$
Percentage of hydrogen $= 9.7\%$
Percentage of oxygen $= 51.6\%$

Required

Empirical formula $= ?$

Solution

Number of gram atoms

Number of gram atoms of element $= \dfrac{\text{Percentage of element}}{\text{Atomic mass of element}}$

Number of gram atoms of carbon $= \dfrac{38.7}{12} = 3.225$ mole

Number of gram atoms of hydrogen $= \dfrac{9.7}{1.008} = 9.6$ mole

Number of gram atoms of oxygen $= \dfrac{51.6}{16} = 3.225$ mole

Atomic ratio

Atomic ratio of element $= \dfrac{\text{No. of gram atoms of element}}{\text{Smallest number}}$

Atomic ratio of carbon $= \dfrac{3.225}{3.225} = 1$

Atomic ratio of hydrogen $= \dfrac{9.6}{3.225} = 3$

Atomic ratio of oxygen $= \dfrac{3.225}{3.225} = 1$

Empirical formula $= CH_3O$

Q17. Serotenin (Molar mass = 176 g mol^{-1}) is a compound that conducts nerve impulses in brain and muscles. It contains 68.2% C, 6.86% H, 15.09% N and 9.08% O. What is its molecular formula?

Ans. Given data

Percentage of carbon $= 68.2\%$
Percentage of hydrogen $= 6.86\%$
Percentage of nitrogen $= 15.09\%$
Percentage of oxygen $= 9.08\%$
Molar mass $= 176\ g\,mol^{-1}$

Required

Molecular formula $= ?$

Solution

Number of gram atoms

Number of gram atoms of element $= \dfrac{\text{Percentage of element}}{\text{Atomic mass of element}}$

Number of gram atoms of carbon $= \dfrac{68.2}{12} = 5.68$ mole

Number of gram atoms of hydrogen $= \dfrac{6.86}{1.008} = 6.80$ mole

Number of gram atoms of nitrogen $= \dfrac{15.09}{14} = 1.08$ mole

Number of gram atoms of oxygen $= \dfrac{9.08}{16} = 0.5675$ mole

Atomic ratio

Atomic ratio of element $= \dfrac{\text{No. of gram atoms of element}}{\text{Smallest number}}$

Atomic ratio of C $= \dfrac{5.68}{0.5675} = 10$

Atomic ratio of H $= \dfrac{6.80}{0.5675} = 12$

Atomic ratio of N $= \dfrac{1.08}{0.5675} = 2$

Atomic ratio of O $= \dfrac{0.5675}{0.5675} = 1$

Empirical formula $= C_{10}H_{12}N_2O$

Molecular formula

Molecular formula $= n \times$ (Empirical formula) .... (i)

Also we k now that

$n = \dfrac{\text{Molecular mass}}{\text{Empirical formula mass}}$

Empirical formula mass $= C_{10}H_{12}N_2O$

$= (12 \times 10) + (1 \times 12) + (14 \times 2) + 16$

$= 176$

$n = \frac{176}{176} = 1$

Putting the value of n = 1 in eq (i)

Molecular formula $= 1 \times (C_{10}H_{12}N_2O)$

Molecular formula $= C_{10}H_{12}N_2O$

Q18. An unknown metal M reacts with S to form a compound with a formula M_2S_3. If 3.12 g of M reacts with exactly 2.88 g of sulphur, what are the names of metal M and the compound M_2S_3?

Ans. Given data

Mass of metal M = 3.12 g

Mass of S = 2.88 g

Required

Name of metal M = ?

Name of compound M_2S_3 = ?

Solution

$$2M + 3S \longrightarrow M_2S_3$$

Number of moles of sulphur $= \frac{\text{Mass of sulphur}}{\text{Atomic mass of sulphur}}$

$= \frac{2.88}{32}$ (Atomic mass of S = 32 g/mol)

Number of moles of S = 0.09 moles

Comparison between moles of S and moles of M

S	:	M
3	:	2
1	:	2/3
0.09	:	2/3 × 0.09
0.09	:	0.06

Number of moles of M = 0.06 moles

Number of moles of M $= \frac{\text{Mass of M}}{\text{Atomic mass of M}}$

0.06 moles $= \frac{3.12 \text{ g}}{\text{Atomic mass of M}}$

Atomic mass of M $= \frac{3.12}{0.06}$

Atomic mass of M $= 52 \text{ g mol}^{-1}$

From the Atomic mass of M, it is clear that

Name of M = **Chromium (Cr)**

Name of M_2S_3 = Cr_2S_3 (Chromium sulphide)

Q19. The octane present in gasoline burns according to the following equation

$$2C_8H_{18(l)} + 25O_{2(g)} \longrightarrow 16CO_{2(g)} + 18H_2O_{(l)}$$

(a) How many moles of O_2 are needed to react fully with 4 moles of octane?

Ans. Given data

Number of moles of octane = 4 moles

Required

Number of moles of O_2 = ?

Solution

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

Comparison between moles of C_8H_{18} and O_2

C_8H_{18}	:	O_2
2	:	25
1	:	25/2
4	:	25/2 × 4
4		50

Number of moles of O_2 : **50 moles**

(b) How many moles of CO_2 can be produced from one mole of octane?

Ans. Given data

Number of moles of octane = 1 mole

Required

Number of moles of CO_2 = ?

Solution

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

Comparison between moles of C_8H_{18} and moles of CO_2

C_8H_{18}	:	CO_2
2	:	16
1	:	16/2
1	:	8

Number of moles of CO_2 : **8 moles**

(c) How many moles of water are produced by the combustion of 6 moles of octane?

Ans. Given data

Number of moles of octane = 6 moles

Required

Number of moles of H_2O = ?

Solution

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

Comparison between moles of C_8H_{18} and moles of H_2O

C_8H_{18}	:	H_2O
2	:	18
1	:	18/2
6	:	18/2 × 6
6	:	54

Number of moles of H_2O : **54 moles**

(d) If this reaction is to be used to synthesize 8 moles of CO_2, how many grams of oxygen are needed? How many grams of octane will be used?

Ans. Given data

Number of moles of CO_2 = 8 moles

Required

Mass of O_2 = ?

Mass of C_8H_{18} = ?

Solution

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

Comparison between moles of CO_2 and moles of O_2

CO_2	:	O_2
16	:	25
1	:	25/16
8	:	25/16 × 8
8	:	12.5

Number of moles of O_2 : **12.5 moles**

Molar Mass of O_2 = $(16 \times 2) = 32\ gmol^{-1}$

Number of moles $= \dfrac{\text{Mass of oxygen}}{\text{Molar mass of oxygen}}$

12.5 moles $= \dfrac{\text{Mass of oxygen}}{32\ gmol^{-1}}$

12.5×32 = Mass of oxygen

400 g = Mass of oxygen

Comparison between moles of CO_2 and moles of C_8H_{18}

CO_2	:	C_8H_{18}
16	:	2
1	:	2/16
8	:	$\frac{2}{16} \times 8$
8	:	1

Number of moles of C_8H_{18} : **1 mole**

Molar Mass of C_8H_{18} $= (12 \times 8) + (1 \times 18) = 114\ gmol^{-1}$

Number of moles of $C_8H_{18} = \dfrac{\text{Mass of } C_8H_{18}}{\text{Molar mass of } C_8H_{18}}$

1 mol $= \dfrac{\text{Mass of } C_8H_{18}}{114\ gmol^{-1}}$

1×114 = Mass of C_8H_{18}

114 g = Mass of C_8H_{18}

Q30. Calculate the number of grams of Al_2S_3 which can be prepared by the reaction of 20g of Al and 30g of sulph How much the non-limiting reactant is in excess?

Ans. Given data

Mass of Aluminium = 20 g

Mass of Sulphur = 30 g

Required

Mass of Al_2S_3 = ?

Non-limiting reactant in excess = ?

Solution

$$2Al + 3S \longrightarrow Al_2S_3$$

Number of moles of reactant

Number of moles of Al $= \dfrac{\text{Mass of Al}}{\text{Atomic mass of Al}}$

Atomic mass of Al $= 27\ gmol^{-1}$

Number of moles of Al $= \dfrac{20}{27} = 0.740$ moles

Number of moles of S $= \dfrac{\text{Mass of S}}{\text{Atomic mass of S}}$

Molar mass of S = 32 g/mol

Number of moles of S $= \dfrac{30}{32} = 0.9375$ moles

Number of moles of product

Comparing number of moles of Al and Al_2S_3

Al	:	Al_2S_3
2	:	1
1	:	1/2
0.740	:	1/2 × 0.740
0.740	:	0.37

Number of moles of Al_2S_3 : 0.37

Comparing number of moles of S and Al_2S_3

S	:	Al_2S_3
3	:	1
1	:	1/3
0.9375	:	1/3 × 0.9375
0.9375	:	0.3125

Number of moles of Al_2S_3 : 0.3125

S is a limiting reactant because it has given less amount of Al_2S_3

Mass of Al_2S_3

Number of moles of $Al_2S_3 = \dfrac{\text{Mass of } Al_2S_3}{\text{Molar mass of } Al_2S_3}$

Molar mass of Al_2S_3 $= (27 \times 2) + (32 \times 3) = 150\ gmol^{-1}$

0.3125 mol $= \dfrac{\text{Mass of } Al_2S_3}{150\ gmol^{-1}}$

0.3125×150 = Mass of Al_2S_3

46.87 g = Mass of Al_2S_3

(ii) $2Al + 3S \longrightarrow Al_2S_3$

Comparison between sulphur and Aluminium

S	:	Al
3	:	2
1	:	2/3
0.937	.	2/3 × 0.937
0.937	:	0.624

Number of moles of Al = 0.624 moles

Excess moles of Al = 0.74 − 0.624

= 0.116 moles

Number of moles of Al $= \dfrac{\text{Mass of Al}}{\text{Atomic mass of Al}}$

Atomic mass of Al $= 27\ g\,mol^{-1}$

0.116 mol $= \dfrac{\text{Mass of Al}}{27\ g\,mol^{-1}}$

0.116×27 = Mass of Al

3.132 g = Mass of Al (Non-limiting reactant in excess)

Q21. A mixture of two liquids, hydrazine N_2H_4 and N_2O_4 are used as a fuel in rockets. They produce N_2 and water vapours. How many grams of N_2 gas will be formed by reacting 100 g of N_2H_4 and 200 g of N_2O_4.

$$2N_2H_4 + N_2O_4 \longrightarrow 3N_2 + 4H_2O$$

Ans. Given data

Mass of N_2H_4 = 100 g

Mass of N_2O_4 = 200 g

Required

Mass of N_2 = ?

Solution

$$2N_2H_4 + N_2O_4 \longrightarrow 3N_2 + 4H_2O$$

Number of moles of reactant

Number of moles of N_2H_4 $= \dfrac{\text{Mass of } N_2H_4}{\text{Molar mass of } N_2H_4}$

Molar mass of N_2H_4 $= (14 \times 2) + (1 \times 4) = 32\ g\,mol^{-1}$

Number of moles of N_2H_4 $= \dfrac{100}{32}$

$= 3.125$ moles

Number of moles of N_2O_4 $= \dfrac{\text{Mass of } N_2O_4}{\text{Molar mass of } N_2O_4}$

Molar mass of N_2O_4 $= (14 \times 2) + (16 \times 4) = 92\ g\,mol^{-1}$

Number of moles of N_2O_4 $= \dfrac{200}{92}$

$= 2.17$ moles

Number of moles of product

Comparing number of moles of N_2H_4 and N_2

N_2H_4	:	N_2
2	:	3
1	:	3/2
3.125	:	$3/2 \times 3.125$
3.125	:	4.68

Number of moles of N_2 : **4.68 moles**

Comparing number of moles of N_2O_4 and N_2

N_2O_4	:	N_2
1	:	3
2.17	:	3×2.17
2.17	:	6.51

Number of moles of N_2 : **6.51 moles**

Hydrazine is a limiting reactant because, it has given less amount of N_2.

Mass of N_2

Number of moles of N_2 $= \dfrac{\text{Mass of } N_2}{\text{Molar mass of } N_2}$

Molar mass of N_2 $= (14 \times 2) = 28\ g\,mol^{-1}$

4.68 mol $= \dfrac{\text{Mass of } N_2}{28\ g\,mol^{-1}}$

4.68×28 = Mass of N_2

131.04 g = Mass of N_2

Q22. Silicon Carbide (SiC) is an important ceramic material. It is produced by allowing sand (SiO_2) to react with carbon at high temperature.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

When 100 kg sand is reacted with excess of carbon, 51.4 kg of SiC is produced. What is the percentage yield of SiC?

Ans. Given data

Mass of SiO_2 = 100 kg

$= 100 \times 1000 = 100{,}000$ g

Mass of SiC = 51.4 kg

$= 51.4 \times 1000 = 51{,}400$ g

Required

Percentage yield of SiC = ?

Solution

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Number of moles of reactant

Number of moles of SiO_2 $= \dfrac{\text{Mass of } SiO_2}{\text{Molar mass of } SiO_2}$

Molar mass of SiO_2 $= 28 + (16 \times 2) = 60\ g\,mol^{-1}$

Number of moles of SiO_2 $= \dfrac{100{,}000\ g}{60\ g\,mol^{-1}}$

Number of moles of SiO_2 = 1666.66 moles

Number of moles of product

Comparing number of moles of SiO_2 and SiC

SiO_2	:	SiC
1	:	1
1666.6	:	1666.6

Number of moles of SiC = 1666.6 moles

Mass of SiC

Number of moles of SiC $= \dfrac{\text{Mass of SiC}}{\text{Molar mass of SiC}}$

Molar mass of SiC $= 28 + 12 = 40\ g\,mol^{-1}$

1666.6 mol $= \dfrac{\text{Mass of SiC}}{40\ \text{gmol}^{-1}}$

1666.6×40 = Mass of SiC

66,666.4 g = Mass of SiC

Percentage yield

Percentage yield of SiC $= \dfrac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$

$= \dfrac{51400}{66,666.4} \times 100$

Percentage yield of SiC = 77%

SOLVED EXAMPLES

Example (1)

A sample of neon is found to consist of $^{20}_{10}Ne$, $^{21}_{10}Ne$, $^{22}_{10}Ne$ in the percentages of 90.92%, 0.26% and 8.82% respectively. Calculate the fractional atomic mass of neon.

Ans. Given data

Mass of ^{20}Ne = 20amu

Mass of ^{21}Ne = 21amu

Mass of ^{22}Ne = 22amu

Percentage of ^{20}Ne = 90.92%

Percentage of ^{21}Ne = 0.26%

Percentage of ^{22}Ne = 8.82%

Required

Fractional atomic mass of Ne = ?

Solution

Average Atomic mass of Ne =

$$\frac{(\text{Mass of }^{20}Ne \times \%\text{ of }^{20}Ne) + (\text{Mass of }^{21}Ne \times \%\text{ of }^{21}Ne) + (\text{Mass of }^{22}Ne \times \%\text{ of }^{22}Ne)}{100}$$

$$= \frac{(20 \times 90.92) + (21 \times 0.26) + (22 \times 8.82)}{100}$$

$$= \frac{1818.4 + 5.46 + 194.04}{100} = \frac{2017.9}{100}$$

= 20.179amu

Fractional Atomic Mass of Ne = 20.179 amu

Example (2)

8.657g of a compound were decomposed into its elements and gave 5.217g of carbon, 0.962g of hydrogen, 2.478g of oxygen. Calculate the percentage composition of the compound under study.

Ans. Given data

Mass of compound = 8.657g

Mass of carbon = 5.217g

Mass of hydrogen = 0.962g

Mass of oxygen = 2.478g

Required

Percentage of carbon = ?

Percentage of hydrogen = ?

Percentage of oxygen = ?

Solution

Formula

Percentage of element $= \dfrac{\text{Mass of element}}{\text{Mass of compound}} \times 100$

Percentage of carbon $= \dfrac{5.217}{8.657} \times 100 =$ **60.26%**

Percentage of hydrogen $= \dfrac{0.962}{8.657} \times 100 =$ **11.11%**

Percentage of oxygen $= \dfrac{2.478}{8.657} \times 100 =$ **28.62%**

The above results tell us that in one hundred gram of the given compound, there are 60.62g of C, 11.11g of H and 28.62g of O.

Example (3)

Ascorbic acid (vitamin C) contains 40.92% carbon, 4.58% hydrogen and 54.5% of oxygen by mass. What is the empirical formula of the ascorbic acid?

Ans. Given data

Percentage of carbon = 40.92%

Percentage of hydrogen = 4.58%

Percentage of oxygen = 54.5%

Required

Empirical formula of Ascorbic acid = ?

Solution:

Number of gram atoms

Number of gram atoms of element $= \dfrac{\text{Percentage of element}}{\text{Atomic mass of element}}$

Number of gram atoms of C $= \dfrac{40.92}{12.0} = 3.41$ gram atoms

Number of gram atoms of H $= \dfrac{4.58}{1.008} = 4.54$ gram atoms

Number of gram atoms of O $= \dfrac{54.5}{16} = 3.406$ gram atoms

Atomic Ratio

Atomic ratio of element $= \dfrac{\text{Number of gram atoms of element}}{\text{Smallest number}}$

Atomic ratio of C $= \dfrac{3.41}{3.406} = 1$

Atomic ratio of H $= \dfrac{4.54}{3.406} = 1.33$

Atomic ration of O $= \dfrac{3.406}{3.406} = 1$

Conversion of atomic ratio into whole numbers

To convert the atomic ratio into whole numbers, multiply with three

C : H : O = 3(1 : 1.33 : 1) = 3 : 4 : 3

Empirical Formula

The above whole number ratio gives us the subscript for empirical formula of the Ascorbic acid

$C_3H_4O_3$

Example (4)

A sample of liquid consisting of carbon, hydrogen and oxygen was subjected to combustion analysis. 0.5439g of the compound gave 1.039g of CO_2, 0.6369g of H_2O. Determine the empirical formula of the compound.

Ans. **Given data**

Mass of organic compound = 0.5439g

Mass of carbon dioxide = 1.039g

Mass of water = 0.6369g

Required

Empirical formula of the compound = ?

Solution

Percentage composition of the sample

$$\text{Percentage of carbon} = \frac{\text{Mass of } CO_2}{\text{Mass of organic compound}} \times \frac{12}{44} \times 100$$

$$= \frac{1.039g}{0.5439g} \times \frac{12.00}{44.00} \times 100 = 52.08\%$$

$$\text{Percentage of hydrogen} = \frac{\text{Mass of } H_2O}{\text{Mass of organic compound}} \times \frac{2.016}{18} \times 100$$

$$= \frac{0.6369g}{0.5439g} \times \frac{2.016}{18} \times 100 = 13.11\%$$

Percentage of oxygen = 100 – (% of C + % of H)

= 100 - (52.08 + 13.11) = 34.77%

Number of gram atoms

$$\text{Number of gram atoms of element} = \frac{\text{Percentage of element}}{\text{Atomic mass of element}}$$

$$\text{Number of gram atoms of C} = \frac{52.08}{12} = 4.34 \text{ gram atoms}$$

$$\text{Number of gram atoms of H} = \frac{13.11}{1.008} = 13.00 \text{ gram atoms}$$

$$\text{Number of gram atoms of O} = \frac{34.77}{16.00} = 2.17 \text{ gram atoms}$$

Atomic ratio

$$\text{Atomic ratio of element} = \frac{\text{number of gram atoms of element}}{\text{Smallest number}}$$

$$\text{Atomic ratio of C} = \frac{4.34}{2.17} = 2$$

$$\text{Atomic ratio of H} = \frac{12.13}{2.17} = 6$$

$$\text{Atomic ratio of O} = \frac{2.17}{2.17} = 1$$

Empirical formula C_2H_6O

Example (5)

The combustion analysis of an organic compound shows it to contain 65.44% carbon, 5.50% hydrogen and 29.06% oxygen. What is the Empirical formula of the compound? If the molecular mass of this compound is 110.15g mol^{-1}. Calculate the molecular formula of the compound.

Ans. **Given data**

Percentage of carbon = 65.44%

Percentage of hydrogen = 5.50%

Percentage of oxygen = 29.06%

Molecular Mass = 110.15g/mole

Required

Empirical formula = ?

Molecular formula = ?

Solution

Number of Gram atoms

$$\text{Number of gram atoms of element} = \frac{\text{Percentage of element}}{\text{Atomic mass of element}}$$

$$\text{Number of gram atoms of C} = \frac{65.44}{12} = 5.45 \text{ gram atoms}$$

$$\text{Number of gram atoms of H} = \frac{5.50}{1.008} = 5.45 \text{ gram atoms}$$

$$\text{Number of gram atoms of O} = \frac{29.06}{16.00} = 1.82 \text{ gram atoms}$$

Atomic ratio

$$\text{Atomic ratio of element} = \frac{\text{number of gram atoms of element}}{\text{Smallest number}}$$

$$\text{Atomic ratio of C} = \frac{5.45}{1.82} = 3$$

$$\text{Atomic ratio of H} = \frac{5.45}{7.82} = 3$$

$$\text{Atomic ratio of O} = \frac{1.82}{1.82} = 1$$

Empirical formula of the compound

C, H and O are present in the compound in the ratio of 3: 3: 1 so the empirical formula C_3H_3O

Molecular formula

In order to determine the molecular formula, first calculate the empirical formula mass.

Empirical formula Mass of $C_3H_3O = 12 \times 3 + 1.008 \times 3 + 16 \times 1 = 55.05 \text{ g mol}^{-1}$

Molecular Mass = 110.15 g mol^{-1}

$$n = \frac{\text{Molecular Mass}}{\text{Empirical formula mass}}$$

$$= \frac{110.15}{55.05} = 2$$

Molecular formula = n × (Empirical formula)

$= 2 \times C_3H_3O$

$= C_6H_6O_2$

Example (6)

Calculate the gram atoms (moles) in

(a) 0.1g of Sodium **(b)** 0.1kg of Silicon

Ans. **Given data**

Mass of Sodium = 0.1g

Mass of Silicon = 0.1kg = 0.1 × 1000 = 100g

Required

(a) Number of gram atoms (moles) of sodium = ?

(b) Number of gram atoms (moles) of silicon = ?

Solution

(a) **Formula**

$$\text{Number of gram atoms} = \frac{\text{Mass of element in grams}}{\text{Atomic mass of element}}$$

Atomic mass of Na = $23\,g\,mol^{-1}$

$$\text{Number of gram atoms of Na} = \frac{0.1\,g}{23\,g\,mol^{-1}} = 0.0043\,moles$$

(b) Atomic mass of Si = $28.086\,g\,mol^{-1}$

$$\text{Number of gram atoms of Si} = \frac{100\,g}{28.086\,g\,mol^{-1}} = 3.56\,moles$$

Example (7)

Calculate the mass of 10^{-3} moles of $MgSO_4$

Ans. **Given data**

Moles of $MgSO_4$ = 10^{-3}

Required

Mass of $MgSO_4$ = ?

Solution

$MgSO_4$ is an ionic compound. We will consider its formula mass in place of molecular mass.

Number of gram formula or

$$\text{Mole of the substance} = \frac{\text{Mass of ionic substance}}{\text{Formula mass of ionic substance}}$$

Formula mass of $MgSO_4$ = $24 + 32 + 16 \times 4$

$= 24 + 32 + 64 = 120\ g\,mol^{-1}$

Applying the formula

$$10^{-3}\,mol = \frac{\text{Mass of } MgSO_4}{120\,g\,mol^{-1}}$$

12×10^{-3} = Mass of $MgSO_4$

0.12g = Mass of $MgSO_4$

Example (8)

How many molecules of water are there in 10.0g of ice? Also calculate the number of atoms of hydrogen and oxygen separately, the total number of atoms and the covalent bonds present in the sample.

Ans. **Given data**

Mass of ice = 10.0g

Required

Number of molecules of water = ?

Number of atoms of hydrogen = ?

Number of atoms of oxygen = ?

Total number of atoms = ?

Total number of covalent bonds = ?

Solution

Number of molecules of water

Formula

$$\text{Number of molecules of } H_2O = \frac{\text{Mass of } H_2O}{\text{Molar mass of } H_2O} \times N_A$$

Molar Mass of H_2O = $2 + 16 = 18\,g\,mol^{-1}$

$$= \frac{10.0}{18} \times 6.02 \times 10^{23}$$

$$= 0.55 \times 6.02 \times 10^{23}$$

$$= 3.31 \times 10^{23} \text{ molecules}$$

Number of molecules of water = **3.31×10^{23} molecules**

Number hydrogen atoms

One molecule of water contains hydrogen atoms = 2

3.31×10^{23} molecules of water contain hydrogen atoms = $2 \times 3.31 \times 10^{23}$

$= 6.62 \times 10^{23}$

Number of oxygen atoms

One molecule of water contains oxygen atom = 1

3.31×10^{23} molecules of water contain oxygen atom = $1 \times 3.31 \times 10^{23}$

$= 3.31 \times 10^{23}$

Total number of atoms of hydrogen and oxygen

$= 6.62 \times 10^{23} + 3.31 \times 10^{23}$

$= 9.93 \times 10^{23}$

Total Number of Covalent Bonds

One molecule of water contains covalent bonds = 2

3.31×10^{23} molecules of water contain covalent bonds = $2 \times 3.31 \times 10^{23}$

$= 6.62 \times 10^{23}$

Example (9)

10.0g of H_3PO_4 has been dissolved in excess of water to dissociate into ions.

Calculate,

(a) Number of molecules in 10.0g of H_3PO_4.

(b) Number of positive and negative ions in case of complete dissociation in water.

(c) Masses of individual ions.

(d) Number of positive and negative charges dispersed in the solution.

Ans. **Given data**

Mass of H_3PO_4 = 10.0g

Molar Mass of H_3PO_4 = $3 + 31 + 64 = 98\,g\,mol^{-1}$

Required

(a) Number of molecules in 10.0g of H_3PO_4 = ?

(b) Number of positive and negative ions in case of complete dissociation in water = ?

(c) Masses of individual ions =

(d) Number of positive and negative charges dispersed in the solution = ?

Solution

(a) Number of molecules

Formula

$$\text{Number of Molecule} = \frac{\text{Mass of } H_3PO_4}{\text{Molar mass of } H_3PO_4} \times N_A$$

$$= \frac{10.0g}{98.0g\ mol^{-1}} \times 6.02 \times 10^{23}$$

$$= 0.102 \times 6.02 \times 10^{23}$$

$$= \mathbf{0.614 \times 10^{23}\ molecules}$$

(b) H_3PO_4 dissolves in water and ionised as follows.

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$$

According to the balance chemical equation

H_3PO_4	:	H^+
1	:	3
6.14×10^{22}	:	$3 \times 6.14 \times 10^{22}$
	:	1.842×10^{23}

Hence, the number of H^+ is $\mathbf{1.842 \times 10^{23}}$

H_3PO_4	:	PO_4^{3-}
1	:	1
6.14×10^{22}	:	6.14×10^{22}

Hence, the number of PO_4^{3-} ions is $\mathbf{6.14 \times 10^{22}}$

(c) Masses of Individual Ions

Mass of positive ions

$$\text{Number of } H^+ = \frac{\text{Mass of } H^+}{\text{ionic mass of } H^+} \times N_A$$

$$1.842 \times 10^{23} = \frac{\text{Mass of } H^+}{1.008} \times 6.02 \times 10^{23}$$

$$\text{Mass of } H^+ = \frac{1.842 \times 10^{23} \times 1.008}{6.02 \times 10^{23}} = 0.308g$$

Mass of H^+ = **0.308g**

Mass of PO_4^{3-} ions

$$\text{Number of } PO_4^{3-} = \frac{\text{Mass of } PO_4^{3-}}{\text{ionic mass of } PO_4^{3-}} \times N_A$$

Ionic Mass of PO_4^{3-} = $31 + 64 = 95\ g\ mol^{-1}$

$$6.14 \times 10^{22} = \frac{\text{Mass of } PO_4^{3-}}{95} \times 6.02 \times 10^{23}$$

Mass of PO_4^{3-} = **9.689g**

(d) Number of positive and negative charges

One molecules of H_3PO_4 positive charges = 3

6.14×10^{22} molecules of H_3PO_4 gives positive charges $= 3 \times 6.14 \times 10^{22}$

$$= 1.842 \times 10^{23}$$

$$= \mathbf{1.842 \times 10^{23}\ positive\ charges}$$

Number of positive and negative charges are always equal.

So number of negative charges = $\mathbf{1.842 \times 10^{23}}$ **negative charges**

Example (10)

A well known ideal gas is enclosed in a container having volume 500 cm^3 at S.T.P. Its mass comes out to be 0.72g. What is the molar mass of this gas?

Ans. **Given data**

Volume of the ideal gas = 500 cm^3

Mass of the ideal gas = 0.72g

Required

Molar mass of the gas = ?

Solution

We can calculate the number of moles of the ideal gas at S.T.P from the given volume.

22.414 dm^3 or 22414 cm^3 of the ideal gas at S.T.P = 1mole

$$1cm^3 \text{ of the ideal gas at S.T.P} = \frac{1}{22414}$$

$$500cm^3 \text{ of the ideal gas at S.T.P} = \frac{1}{22414} \times 500$$

$$= 0.0223 \text{ moles}$$

We know that

$$\text{Number of moles of gas} = \frac{\text{Mass of the gas}}{\text{Molar mass of the gas}}$$

$$0.0223 \text{ mole} = \frac{0.72g}{\text{Molar mass of the gas}}$$

$$\text{Molar mass of the gas} = \frac{0.72g}{0.0223\ mole}$$

Molar mass of the gas = $\mathbf{32\ g\ mol^{-1}}$

Example (11)

Calculate the number of grams of K_2SO_4 and water produced when 14g of KOH are reacted with excess of H_2SO_4. Also calculate the number of molecules of water produced.

Ans. **Given data**

Mass of KOH = 14g

Molar mass of KOH = 39 + 16 + 1 = 56 $g\ mol^{-1}$

Required

Number of grams (Mass) of K_2SO_4 = ?

Mass of H_2O = ?

Number of molecules of H_2O = ?

Solution

$$\text{Number of moles of KOH} = \frac{\text{Mass of KOH}}{\text{Molar mass of KOH}}$$

$$= \frac{14.0g}{56g/mole} = 0.25 \text{moles}$$

Equation

$$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$$

Comparison between Number of moles of KOH and K_2SO_4

KOH	:	K_2SO_4
2	:	1
1	:	$\frac{1}{2}$

$$0.25 : \frac{1}{2} \times 0.25$$
$$0.25 : 0.125$$

Number of moles of K_2SO_4 = 0.125mole

$$\text{Number of moles of } K_2SO_4 = \frac{\text{Mass of } K_2SO_4}{\text{Molar mass of } K_2SO_4}$$

Molar Mass of $K_2SO_4 = 39 \times 2 + 32 + 16 \times 4$
$= 78 + 32 + 64 = 174\ g\,mol^{-1}$

$$0.125 \text{ moles} = \frac{\text{Mass of } K_2SO_4}{174 g\,mol^{-1}}$$

0.125×174 = Mass of K_2SO_4

21.75g = Mass of K_2SO_4

Comparison between number of moles of KOH and H_2O

KOH	:	H_2O
2	:	2
1	:	1
0.25	:	0.25

Number of moles of H_2O = 0.25moles

$$\text{Number of moles of } H_2O = \frac{\text{Mass of } H_2O}{\text{Molar mass of } H_2O}$$

Molar mass of $H_2O = 2 + 16 = 18\ g\,mol^{-1}$

$$0.25 \text{ moles} = \frac{\text{Mass of } H_2O}{18 g\,mol^{-1}}$$

0.25×18 = Mass of H_2O

4.5 g = Mass of H_2O

Number of molecules of H_2O

Number of molecules of H_2O = Number of moles of $H_2O \times N_A$
$= 0.25 \times 6.02 \times 10^{23}$
$= 1.505 \times 10^{23}$ molecules

Number of molecules of H_2O = 1.55×10^{23} molecules

Example (12)

Mg metal reacts with HCl to give H_2 gas. What is the minimum volume of HCl solution (27% by Mass) required to produce 12.1g of H_2? The density of HCl solution is 1.14g cm^{-3}.

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2\,(aq)} + H_{2\,(g)}$$

Ans.

Given data

Mass of H_2 produced = 12.1g
Density of HCl solution = 1.14gcm^{-3}
Percentage of HCl solution = 27%

Required

Volume of HCl solution = ?

Solution

First of all convert the Mass of H_2 into moles, then compare the moles of H_2 and moles of HCl according to balance chemical equation.

Formula

$$\text{Number of moles of } H_2 = \frac{\text{Mass of } H_2}{\text{Molar mass of } H_2}$$

Molar Mass of $H_2 = 2.016\ g\,mol^{-1}$

$$\text{Number of moles of } H_2 = \frac{12.1g}{2.016\ g\,mol^{-1}} = 6\text{mole}$$

Equation

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2\,(aq)} + H_{2\,(g)}$$

Comparison between Number of Moles of H_2 and HCl

H_2	:	HCl
1	:	2
6	:	2×6
6		12

Moles of HCl = 12 moles

Molar Mass of HCl = 1 + 35.5 = 36.5 $g\,mol^{-1}$
Mass of HCl = Number of Moles of HCl × Molar Mass of HCl
= 12 moles × 36.5 $g\,mol^{-1}$ = 438g

Mass of HCl = 438grams

We know that the percentage of HCl = 27% by weight, it means that 27g of HCl are present in HCl solution = 100g

1g of HCl is percent in HCl solution $= \frac{100}{27}$ g

438 of HCl are present in HCl solution $= \frac{100}{27} \times 438$
= 1622 2g

$$\text{Volume of HCl} = \frac{\text{Mass of HCl solution}}{\text{Density of HCl}}$$

$$\text{Volume of HCl} = \frac{1622.2g}{1.14g\,cm^{-3}}$$
$= 1422.98\ cm^3$

Example (13)

NH_3 gas can be prepared by heating together two solids, NH_4Cl and $Ca(OH)_2$. If a mixture containing 100g of each solid is heated then

(a) Calculate the number of grams of NH_3 produced (b) Calculate the excess amount of reagent left unreacted

$$2NH_4Cl_{(s)} + Ca(OH)_{2(s)} \rightarrow CaCl_{2(s)} + 2NH_{3(g)} + 2H_2O_{(l)}$$

Ans. Given data

Mass of NH_4Cl = 100g
Mass of $Ca(OH)_2$ = 100g

Required

(a) Number of grams (mass) of NH_3 = ?
(b) Excess amount of reagent left unreacted = ?

Solution:

Number of moles of reactants

Formula

$$\text{Number of moles} = \frac{\text{Mass in grams}}{\text{Molar mass}}$$

Molar mass of $NH_4Cl = 14 + 4 + 35.5 = 53.5\,g\,mol^{-1}$

Number of moles of $NH_4Cl = \dfrac{100g}{53.5\,g\,mol^{-1}} = 1.87mole$

Molar mass of $Ca(OH)_2 = 40 + 16 \times 2 + 2$

$= 40 + 32 + 2 = 74\,g\,mol^{-1}$

Number of moles of $Ca(OH)_2 = \dfrac{100g}{74\,g\,mol^{-1}} = 1.35mole$

Number of moles of product (NH_3)

Equation

$$2NH_4Cl_{(s)} + Ca(OH)_{2(s)} \rightarrow CaCl_{2(s)} + 2NH_{3(g)} + 2H_2O_{(l)}$$

Comparison between number of moles of NH_4Cl and NH_3

NH_4Cl	:	NH_3
2	:	2
1	:	1
1.87	:	1.87

Number of moles of NH_3 = 1.87 moles

Comparison between number of moles of $Ca(OH)_2$ and NH_3

$Ca(OH)_2$	:	NH_3
1	:	2
1.35	:	2 × 1.35
1.35	:	2.70

Number of moles of NH_3 = 2.70 moles

Since the number of moles of NH_3 produced by 100g of NH_4Cl are less, so NH_4Cl is the limiting reactant. The other reactant, $Ca(OH)_2$ is present in excess.

Hence

Mass of NH_3 produced = 1.87moles × $17gmol^{-1}$

= 31.179g

(b) Amount of the reagent present in excess

To calculate the amount of the reagent present in excess compare the moles of NH_4Cl and $Ca(OH)_2$

NH_4Cl	:	$Ca(OH)_2$
2	:	1
1	:	$\frac{1}{2}$
1.87	:	1/2 × 1.87
1.87	:	0.935

Hence the number of moles of $Ca(OH)_2$ which completely react with 1.87 moles of NH_4Cl is 0.935 moles.

Number of moles of $Ca(OH)_2$ taken = 1.35 moles

Number of moles of $Ca(OH)_2$ used = 0.935moles

Number of moles of $Ca(OH)_2$ left behind = 1.35 − 0.935

= 0.415

Mass of $Ca(OH)_2$ left unreacted (excess) = 0.415 × 74

= 30.71g

Excess amount of $Ca(OH)_2$ left unreacted = 30.71g

Example (14)

When lime stone $CaCO_3$ is roasted, quicklime (CaO) is produced according to following equation. The actual yield of CaO is 2.5kg, when 4.5kg of lime stone is roasted. What is the percentage yield of this reaction.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

Ans. **Given data**

Mass of limestone roasted = 4.5kg = 4.5 × 1000 = 4500g

Mass of quick lime (actual yield) = 2.5kg = 2.5 × 1000 = 2500g

Molar Mass of $CaCO_3 = 40 + 12 + 16 \times 3$

$= 40 + 12 + 48 = 100\,g\,mol^{-1}$

Molar mass of $CaO = 40 + 16 = 56\,g\,mol^{-1}$

Required

Percentage yield of CaO = ?

Solution

Equation

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

According to balanced chemical equation

100g of $CaCO_3$ give CaO = 56g

1g of $CaCO_3$ gives CaO $= \dfrac{56}{100}g$

4500g of $CaCO_3$ give CaO $= \dfrac{56}{100} \times 4500 = 2520g$

Theoretical yield of CaO = 2520g

Actual yield of CaO = 2500g

Percentage yield $= \dfrac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$

$= \dfrac{2500}{2520} \times 100$

= 99.2%

% yield of CaO = 99.2%

Additional Questions

Q. In industry, costly reactant is always taken as limiting reactant.

Ans. In industry, costly reactant is taken in small amounts and cheaper one in excess. As a result of that costly reactant is completely consumed earlier. Hence, its amount is not wasted. Due to which reaction becomes economical and there is no financial loss of costly reactant.

Q. Differentiate between qualitative and quantitative analysis.

Ans.

Qualitative Analysis	Quantitative Analysis
The analysis which is made to identify different elements present in the compound is called as qualitative analysis.	The analysis which is made to determine the exact amount of each element present in the compound is called as quantitative analysis.
It is the initial analysis to detect the elements present in the compound.	By this analysis we can calculate the %age of element present in the compound.
e.g. Salt analysis, detection of elements and functional groups.	e.g. Volumetric analysis, combustion analysis, gravimetric analysis.

Q. In combustion analysis, why the %age of oxygen cannot be measured directly?

Ans. In combustion analysis, a known amount of organic compound is burnt in free supply of oxygen. The carbon and hydrogen of the organic compound is converted into CO_2 and H_2O respectively. But as oxygen gas is also provided from the external source to burn the organic compound, so we cannot measure the %age of oxygen present in the compound directly. However it is determined by method of difference.

$$\%\text{ age of O} = 100 - (\%\text{age of C} + \%\text{age of H})$$

Q. How can we calculate the efficiency of a chemical reaction?

Ans. The efficiency of a chemical reaction is calculated in the term of % age yield. "Percentage yield is defined as: it is the ratio of the actual yield to the theoretical yield multiplied by 100."

$$\%\text{ age yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Greater the % age yield of a chemical reaction, more amount of product is formed. Hence greater the efficiency of the reaction.

Q. What is a Compound?

Ans. A substance formed by the reaction of two or more chemical elements. The elements in a compound are present in fixed ratios. For example pure water is a compound made from two elements - hydrogen and oxygen. The fixed ratio of hydrogen to oxygen in water is 2:1. Each molecule of water contains two hydrogen atoms bonded to a single oxygen atom.

Compounds can be decomposed chemically into their constituent elements.

Q. The Term formula mass is used for ionic compounds instead of molecular mass.

Ans. The term formula Unit is used for the ionic compounds as represented in their empirical formula. And the sum of atomic masses of elements in the formula unit is called formula mass e.g Formula Unit of sodium chloride is NaCl and formula mass is 58.5g/ mole. The term molecular mass is used for molecular compounds e.g. H_2O.

Important Previous Board Questions

- **Q.** How does a limiting reactant control the amounts of products formed?
- **Q.** How can the efficiency of a chemical reaction be expressed?
- **Q.** Concept of limiting reactant is not applicable to the reversible reactions. Explain it.
- **Q.** The atomic masses may be in fractions. Why?
- **Q.** What is the function of electrometer in mass spectrometer?
- **Q.** Which laws are to be considered during stoichiometric calculations?
- **Q.** What is the justification of two strong peaks in mass spectrum of bromine?
- **Q.** Amount of products formed during a chemical reaction; depend upon the amount of limiting reactant. Justify.
- **Q.** Explain formation of ions with respect to energy changes.
- **Q.** Give the applications of limiting reactant.
- **Q.** Why the isotopes have same chemical properties?

For Answers study Scholar's CHEMISTRY (Objective) XI

Chapter 2

EXPERIMENTAL TECHNIQUES IN CHEMISTRY

Analytical Chemistry

"The branch of chemistry which deals with the chemical characterization (qualitative and quantitative analysis) of a compound is called analytical chemistry."

Major steps involved in quantitative analysis of a compound

Following major steps are necessary for complete quantitative analysis of a compound

i. Obtaining a sample for analysis,
ii. Separation of the desired constituent.
iii. Measurement and calculation of results.
iv. Drawing conclusion from the analysis.

SEPARATION TECHNIQUES

FILTRATION

"The process in which insoluble particles (suspended particles or precipitates) are separated from liquids is called filtration."

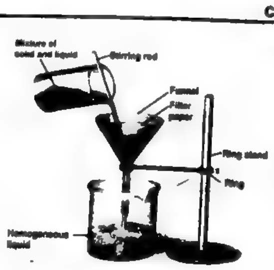
Filter media

Filtration can be performed with several types of filter media. Nature of the precipitate and other factors dictate which filter medium must be used. Following filter media are frequently used for filtration.

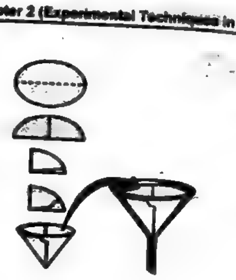
- Filter paper
- Paper pulp
- Filter crucibles
- Cloth
- Cotton
- Sand

Filtration through filter paper

1. Filtration by a glass funnel and filter paper is usually a slow process. As the mixture is poured onto the filter paper, the solvent (water) passes through leaving behind the suspended particles on the filter paper.
2. Filter papers are available in variety of porosites (pore sizes). Which pore size is to be used, depends upon the size of the particles in the precipitate.
3. The filter paper should be large enough so that it is one-fourth to one-half full of precipitate at the end of filtration. The funnel should be large enough for its rim to extend 1 to 2 cm above the top circumference of the paper.
4. If the process of filtration is to run smoothly, the stem of the funnel should remain continuously full of liquid as long as there is liquid in the conical portion.
5. The stem of funnel should be several inches long so that it can extend a few centimeters down into the receiving beaker and tip should touch the side of the beaker. In this way, the filtrate runs down the side of beaker without splashing.



Filtration assembly



Filtration assembly

Folding of filter paper

The folding of filter paper is important and following points should be kept in mind:

- The paper should be folded twice. The first fold should be along the diameter of the paper. The second fold should be such that the edges do not quite match.
- The paper should be opened on the slightly larger section. This provides a cone with three-fold thickness halfway around and one thickness the other halfway around and an apex angle very slightly greater than 60°.
- The paper may then be inserted into 60° funnel, moistened with water and firmly pressed down.

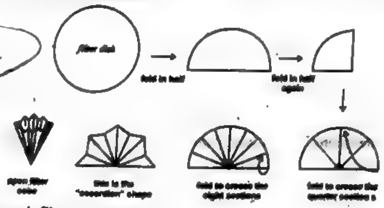
Suction and Rate of Filtration

The filtering operation could be very time consuming if it were not aided by a gentle suction as liquid passes through stem. This suction cannot develop unless the paper fits tightly all around its upper circumference.

Fluted filter paper

The rate of filtration through conical funnel can be considerably increased by using fluted filter paper. For preparation of such a paper ordinary filter paper is folded in such a way that a fan like arrangement with alternate elevations and depressions at various folds is obtained. In this way, we increase the surface area of filter paper. As a result, the rate of filtration increases.

Q. Rate of filtration can be increased by using fluted filter paper. Justify.



Filtration through filter crucibles

This is a convenient way to filter a precipitate by suction through a crucible. Two types of crucibles are generally used.

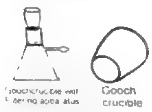
porcelain porcelain

Gooch crucible

- It is made up of porcelain.
- It has a perforated bottom which is covered with paper pulp or a filter paper cut to its size.

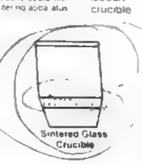
Q. Differentiate between Gooch crucible and sintered glass crucible.

- Quick filtration can be done by placing the crucibles in a suction filtering apparatus
- It is useful for the filtration of precipitates, which need to be ignited at higher temperature
- If its perforations are covered with asbestos mat then it may be used to filter solutions that react with paper e.g. concentrated HCl, $KMnO_4$ (alkaline) solutions etc



Sintered glass crucible

- It is a glass crucible with a porous glass disc sealed into the bottom
- No need to place any kind of filter paper in its bottom
- It is very convenient to use sintered glass crucible because no preparation is needed as with the Gooch crucible.



CRYSTALLIZATION

"Crystallization is the removal of a solid from solution by increasing its concentration above the saturation point in such a manner that the excess solid separates out in the form of crystals."

Principle

The basic principle of crystallization is that solute should be soluble in a suitable solvent at high temperature and excess amount of solute is thrown out as crystals when it is cooled.

Q. Why NaCl cannot be purified by crystallization?

Steps involved in crystallization

The process of crystallization involves the following steps

1. Choice of a solvent
2. Preparation of the saturated solution
3. Filtration
4. Cooling
5. Collecting the crystals
6. Drying the crystals
7. Decolourization of undesirable colours.

Q9. Write down the main characteristics of a solvent selected for crystallization of a compound.

(1) Choice of solvent

The solvent is chosen on hit and trial basis. It is necessary to try a number of solvents before arriving at a conclusion

Characteristics of an ideal solvent

(i) It should dissolve a large amount of the substance (solute) at its boiling point and only a small amount at the room temperature
(ii) It should not chemically react with solute.
(iii) It should either not dissolve the impurities or impurities should not be crystallize from it along with the solute
(iv) ~~On cooling~~, it should deposit well-formed crystals of the pure compound
(v) It should be inexpensive
(vi) It should be safe to use and should be easily removable

Mostly used solvents

The solvents which are mostly used for crystallization are

• Water (H_2O)	• Rectified spirit (95% ethanol)	• Absolute ethanol
• Acetone (CH_3COCH_3)	• Acetic acid (CH_3COOH)	• Chloroform ($CHCl_3$)
• Carbon tetrachloride (CCl_4)	• Petroleum ether	• Diethyl ether ($C_2H_5OC_2H_5$)

Combination of Solvents

[illegible] none of the solvents is found suitable for crystallization, a combination of two or more miscible solvents may be employed.

Precautionary Measures

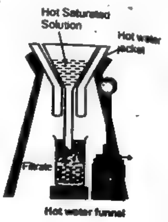
If the solvent is inflammable then precaution should be taken while heating the solution so that it does not catch fire. In such cases, water bath is used for heating purpose.

(2) Preparation of the saturated solution

- After selecting a suitable solvent, the substance is then dissolved in a minimum amount of solvent and is heated directly or on a water bath with constant stirring.
- Add more solvent to the boiling solution if necessary until all the solute has dissolved.

(3) Filtration

- The insoluble impurities in saturated solution are then removed by filtering the hot saturated solution, through a normal or fluted filter paper.
- This avoids the premature crystallization of the solute on the filter paper or in the funnel stem.
- If necessary hot water funnel should be used for this purpose.



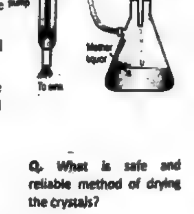
Hot water funnel

(4) Cooling

- The hot filtered solution is then cooled at a moderate rate so that medium sized crystals are formed.
- Slow cooling yields bigger crystals which are likely to include considerable amount of solvent carrying impurities with it and complicating the drying process.

(5) Collecting the Crystals

Filtration: When the crystallization is complete, the mixture of crystals and the mother liquor is filtered through a Gooch crucible using a vacuum pump. Full suction is applied in order to drain the mother liquor from the crystals as effectively as possible.



Pressing: When the filter cake is rigid enough, it is pressed firmly with a cork to drain the left-over liquid.

Washing: The crystals are then washed with a small portion of cold solvent and the process is repeated for several times.

Evaporation: The mother liquor is quite often concentrated by evaporation and cooled to obtain a fresh crop of crystals.

Success of Operation: The process of crystallization appears to be very simple yet the success of operation lies in the amount or percentage of crystallized product obtained from the crude substance.

(6) Drying of crystallized substance

Q. What is safe and reliable method of drying the crystals?

(i) Through filter paper

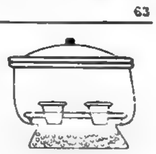
Pressing it between several folds of filter papers and repeating the process several times dries the crystallized substance. This process has the disadvantage that the crystals are crushed to a fine powder and sometimes the fibres of filter paper contaminate the product.

(ii) Drying in an oven

The crystals are dried in an oven provided the substance does not melt or decompose on heating at 100°C.

(iii) Vacuum Desiccator

A safe and reliable method of drying crystals is through a vacuum desiccator. In this process, crystals are spread over a watch glass and kept in vacuum desiccator for several hours. **Drying agents** used in a desiccator are $CaCl_2$, silica gel or phosphorous pentaoxide (P_2O_5) [con. H_2SO_4 also].


Simple Desiccator

Silica gel is prepared by acidification of sodium silicate with sulphuric acid followed by washing with water and drying.

(7) Decolourization of Undesirable Colours

Sometimes during the preparation of a crude substance, the colouring matter or resinous products affect the appearance of product and it may appear coloured. Such impurities are conveniently removed by boiling the substance in the solvent with sufficient quantity of **finely powdered animal charcoal** and then filtering the hot solution. The coloured impurities are **adsorbed** by animal charcoal and the pure decolourized substance crystallizes out from the filtrate on cooling.

Q. How coloured impurities are removed from crude substance during crystallization

Q.4 Why is there a need to crystallize the crude product?

Ans. The preparation of chemical compounds usually affords a crude product. The crude product may contain soluble and insoluble impurities. Insoluble impurities are removed by filtration while soluble impurities are removed by crystallization process. Crystallization also gives a definite geometrical shape to the crystals of the crude product. So in order to get pure product in the form of crystals there is a need to crystallize the crude product.

SUBLIMATION

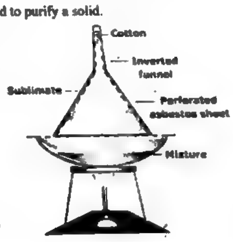
"The process in which a solid, when heated vapourizes directly without passing through the liquid phase and these vapours can be condensed to form the solid again is called sublimation."

$$\text{Solid} \rightleftharpoons \text{Vapours}$$

This endothermic phase transition occurs at temperatures and pressures below the triple point.

Example: Dry ice is solid carbon dioxide. At room temperature and pressure, it sublimates into carbon dioxide vapour.

- It is frequently used to purify a solid.



Examples

Benzoic acid, naphthalene, iodine (I_2), ammonium chloride (NH_4Cl), dry ice (solid CO_2) etc.

Sublimand

The solid substance which is being sublimed is called sublimand.

Sublimate

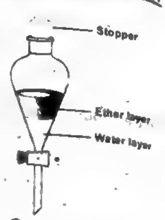
The pure solid obtained after sublimation is called sublimate.

Sublimation process

To carry out the process, the substance is taken in watch-glass, covered with an inverted funnel. The substance is then slowly heated over a sand bath and funnel [illegible] wet cotton. The pure solid deposits on the inner side of funnel.

SOLVENT EXTRACTION

"It is a technique in which a solute can be separated from a solution by shaking the solution with a solvent in which the solute is more soluble and the added solvent does not mix with the solution."



Separating funnel

Characteristics

The main characteristics of solvent extraction are as follows

- It is an equilibrium process and follows the distribution law.
- This technique is particularly useful when the product is volatile or thermally instable.
- It is a convenient technique and is carried out in separating funnel.

Distribution Law / Partition Law

"A solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added."

Applications of distribution law

(i) Solvent extraction

(ii) Liquid-phase chromatography

Distribution co-efficient

"The ratio of concentration of solute dissolved in two immiscible liquids at equilibrium is called distribution coefficient."

$$K = \frac{\text{Concentration of solute in organic phase}}{\text{Concentration of solute in aqueous phase}}$$

Process

Solvent extraction is an important technique in chemical analysis. Usually, it is done by placing the solution and the second liquid into a separating funnel. The funnel is stoppered and the two liquids are shaken together.

Ether Extraction

The most common laboratory example of solvent extraction is ether extraction. This is used to separate products of organic synthesis from water. In a typical organic synthesis, the aqueous solution containing the organic product is shaken up with ether in a separating funnel and allowed to separate. The inorganic impurities remain in aqueous phase whereas the organic compound goes to the ether layer. The ether layer is separated and the organic compound is obtained by evaporating the ether

Efficiency of the process

Repeated extractions by using small portions of solvent are more efficient than using a single but larger volume of solvent.

Carbon Tetrachloride (CCl_4) Extraction

The distribution of iodine between two immiscible solvents, water in the presence of KI and CCl_4. Iodine reacts with iodide ion to produce tri-iodide ion in a reversible reaction. The following dynamic equilibrium is established.

$$I_2 + I^{-1}_{(aq)} \rightleftharpoons I^{-1}_{3(aq)}$$

Soluble in CCl_4 Soluble in water

At this point, the rate at which iodine passes from CCl_4 to water equals the rate at which it passes from water to CCl_4.

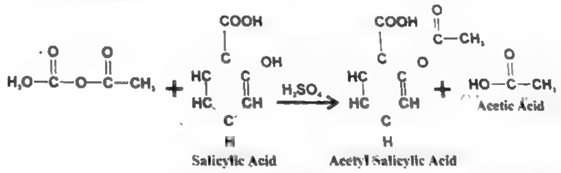
So, if we add CCl_4 to an aqueous solution of I_3^- ions, the iodine will transfer from the aqueous layer into organic layer. As a result, the brown colour of tri-iodide ions fades and the purple colour of free iodine molecules appears in organic phase. To achieve a good separation, the two liquids are gently shaken to increase their area of contact and improve the chances of transferring iodine molecules. No matter how much iodine is used, the ratio of the final concentrations at equilibrium is constant. The constant is called distribution coefficient, K and is given by

$$K = \frac{[I_2(CCl_4)]}{[I_{2(aq)}]}$$

At 25°C, the value of "K" for this equilibrium is 85. This means that the concentration of iodine in CCl_4 is 85 times more than in water

Q5. A water insoluble organic compound aspirin is prepared by the reaction of salicylic acid with a mixture of acetic acid and acetic anhydride. How will you separate the product from the reaction mixture?

Ans. The statement indicates that aspirin is insoluble in water so we can put the reaction mixture in ice chilled water while stirring. Aspirin separates in the form of white precipitates which can be filtered by specific filtration technique (particle size is very small). Aspirin comes out as residue on filter media while filterate contains the reaction mixture with water



Salicylic Acid Acetyl Salicylic Acid

Q6. A solid organic compound is soluble in water as well as in chloroform. During its preparation, it remains in aqueous layer. Describe a method of separation?

Ans. It is evident that organic compound is more soluble in chloroform than in water. So during the preparation of organic compound, if it remains in aqueous layer, then it can be separated by solvent extraction using a separating funnel. Organic compound leaves the aqueous layer and comes in chloroform after shaking, leaving behind the impurities in water. (according to distribution law). Separate the organic layer and evaporate it, organic compound is obtained

Q7. In solvent extraction technique, why repeated extraction using small portions of solvent are more efficient than using a single extraction but larger volume of solvent.

Ans. According to Distribution law

"A solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added."

In a single extraction using larger amount of solvent, a little amount of solute is extracted out, so extraction is less efficient. While in repeated extractions, solute is extracted out to a greater extent by using smaller amount of fresh solvent

So repeated extractions are more efficient, as recovery of solute is greater.

CHROMATOGRAPHY

"It is a technique of separation in which components of a mixture are separated on the basis of their relative affinities for stationary and mobile phases."

Meanings

The word chromatography originates from the Greek word "Khromatos" meaning "colour writing". This is because the earliest chromatographic methods were confined to separation of coloured substances from their mixture.

- The eluate is the mobile phase leaving the column
- The eluent is the solvent that will carry the analyte
- **Elution:** It is the tendency of solutes to dissolve and move with the mobile phase

Phases in chromatography

Chromatography involves the distribution of a solute between two phases

(i) Stationary Phase

It may be a solid or a liquid supported as a thin film on the surface of an inert solid.

Examples

Alumina, silica gel, silica, charcoal, filter paper, acetone, water, ethyl alcohol etc.

(ii) Mobile Phase (Moving Phase)

It may be a liquid or a gas. If flows over the surface of the stationary phase While passing over the stationary phase, it competes with it for the components of the mixture.

Examples

Acetone, water, ethyl alcohol, benzene, H_2 gas, N_2 gas etc.

Distribution Coefficient (K)

The distribution of the components of a mixture between two phases is governed by distribution coefficient (K) which is

$$K = \frac{\text{Concentration of a component in the moving phase}}{\text{Concentration of that component in the stationary phase}}$$

There are two possibilities for the value of 'K'.

(i) The component with a greater value of 'K' remains largely dissolved in the mobile phase and passes over the stationary phase quickly.

(ii) The component with a small value of 'K' mostly remains in the stationary phase as the mobile phase follows over it.

Differences between Adsorption and Partition Chromatography

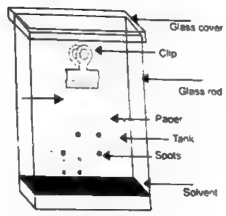
Adsorption Chromatography	Partition Chromatography
The chromatography in which the stationary phase is a solid is called adsorption chromatography."	The chromatography in which the stationary phase is a liquid is called partition chromatography
In this type, a substance leaves the mobile phase to become adsorbed on the surface of solid stationary phase. **Examples** • Column chromatography • Thin layer chromatography • Gas solid chromatography	In this type, the substances being separated are distributed throughout both the stationary and mobile phases. **Examples** • Paper chromatography • Gas liquid chromatography

PAPER CHROMATOGRAPHY

- It is a technique of **partition chromatography**
- Here the **stationary phase** is a liquid (say H_2O) adsorbed on paper. The adsorbed water behaves as an immiscible liquid towards the mobile phase, which passes over the paper.
- The **mobile phase** is usually an organic liquid.
- There are three common ways of carrying out paper chromatography namely

(i) Descending **(ii) Ascending** **(iii) Radial /circular**

113
66



Paper chromatography

Ascending Paper Chromatography

- In this technique, the solvent is in a pool at the bottom of a vessel in which the paper is supported and the solvent travels upwards by capillary action.
- A solvent mixture, specially composed in accordance with the sample to be separated, is poured into the chromatographic tank. Cover the tank to homogenise its inner atmosphere.
- Take about 20 cm strip of Whatmann's Chromatographic paper No. 1 and draw on it a thin pencil line about 2.5 cm from one end.
- Spot a point, on the pencil line, with the sample mixture solution. To facilitate identification of the components of the mixture, spots of the known compounds may also be placed alongside.
- When the spots have dried, suspend the paper with clips so that the impregnated end dips into the solvent mixture to depth of 5-6 mm.
- Cover the tank. As the solvent front passes the spots, the solutes begin to move upward
- The rate at which they move depends on their distribution coefficients. When the solvent front has risen to about $\frac{3}{4}$ of the length of the paper, remove the strip, mark the solvent front with a pencil and allow the strip to dry

Chromatogram

"The finished dried product with the colour bands of various components of a mixture obtained in chromatographic experiment is called chromatogram."

- The different components of the mixture, if coloured, can visually be identified.

Development of chromatogram

If the components of a mixture are colourless, then the chromatogram has to be developed by.

(i) Chemical Methods

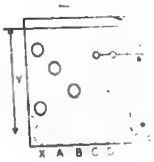
By using locating agents such as H_2S, ninhydrin and rubeanic acid etc.

(ii) Physical Methods

By heating or by throwing ultra violet radiations, we can identify the spots.

Retardation Factors (R_f)

"It is the mathematical ratio which is obtained by dividing distance travelled by a component from original spot and the distance travelled by the solvent from original spot."



$$R_f = \frac{\text{Distance travelled by a component from the original spot}}{\text{Distance travelled by solvent from the original spot}}$$

$$R_f(A) = \frac{x}{y} \qquad R_f(B) = \frac{z}{y}$$

- Each component of a mixture has specific R_f value
- The R_f value has no units
- The R_f value of a component is related to its distribution coefficient

Uses of Chromatography

(i) The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of products

(ii) They are equally important in qualitative and quantitative analysis.

(iii) This technique is used for the determination of the purity of a substance.

(iv) It is important for Forensic analysis

Exercise Q7. The following figure shows a developed chromatogram on paper with five spots

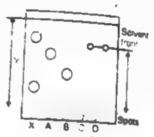
(i) Unknown mixture X

(ii) Sample A

(iii) Sample B

(iv) Sample C

(v) Sample D



Find out

(I) Composition of X.

(II) Which sample is impure with its composition?

Ans. (I) Composition of X

X contains two spots indicating that it contains two substances. If we compare the distances covered by spots, we will observe that sample B and C has the spot with equal distance covered as the mixture X. So X contains B and C samples.

(II) Impure sample with its composition

All the samples have one spot except D. So it is concluded that D is an impure substance. By comparing the distances covered, it is observed that D contains A and C samples.

KEY POINTS

1) A complete characterization of a compound must include both qualitative and quantitative analyses.
2) A complete quantitative analysis of a compound generally involves four major steps.
3) The process of filtration is used to separate insoluble particles from liquids and it can be performed with several types of filter media
4) If the process of filtration with the filter paper is to run smoothly, the stem of the funnel should remain continuously full of liquid as long as there is liquid in the conical portion.
5) The filtering operation with the filter paper could be very time consuming if it were not aided by a gentle suction as liquid passes through the stem. This suction cannot develop unless the paper fits tightly all around the upper circumference of the funnel.
6) The rate of filtration can be considerably increases by using a fluted filter paper.
7) A crystalline solid compound is purified by crystallization from a suitable solvent. A solvent for crystallization should be able to dissolve the solute at high temperature and the maximum amount of the solute should be thrown out by the solvent when the solution is cooled. The process of crystallization involves many steps.

8) The process of sublimation involves converting a solid directly into vapours and these vapours are then condensed to form solid again. It is frequently used to purify a solid.
9) Solvent extraction technique involves the separation of a solute from a solution by shaking it with an immiscible solvent in which the solute is more soluble. The technique is mostly applied to separate organic compounds from water
10) Repeated extractions using small portions of solvent are more efficient than using a single extraction but large volume of solvent.
11) Solvent extraction is an equilibrium process and it is controlled by distribution law. The technique is particularly useful when the compound to be separated is volatile or thermally unstable
12) Chromatography is a technique used for separating the components of a mixture. These components are distributed between a stationary and a mobile phase. The stationary phase may be a solid or a liquid supported on a solid. It adsorbs the mixture under separation. The mobile phase may be a liquid or a gas and while passing over the stationary phase, competes with it for the constituents of the mixture.
13) In paper chromatography, the stationary phase is water adsorbed on paper. The mobile phase is usually an organic liquid.
14) The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of the products.

SOLVED OBJECTIVE EXERCISE

Q1 **Multiple choice questions**

(i) A filtration process could be very time consuming if it were not aided by a gentle suction which is developed

(a) if the paper covers the funnel upto its circumference.
(b) if the paper has got small sized pores in it.
(c) if the stem of funnel is large so that it dips into the filtrate.
(d) if the paper fits tightly.

(ii) During the process of crystallization, the hot saturated solution

(a) is cooled very slowly to get large sized crystals.
(b) is cooled at moderate rate to get medium sized crystals.
(c) is evaporated to get the crystals of product.
(d) is mixed with an immiscible liquid to get the pure crystals of product.

(iii) Solvent extraction is a technique which is controlled by

(a) law of mass action (b) amount of solvent
(c) distribution law (d) the amount of solute

(iv) Solvent extraction technique is particularly useful technique for the separation when the product to be separated is

(a) non volatile or thermally unstable. (b) volatile or thermally stable.
(c) non volatile or thermally stable. (d) volatile or thermally unstable.

(v) The comparative rates at which the solute moves in paper chromatography depend upon

(a) the size of paper (b) R_f value of solute
(c) temperature of experiment (d) size of chromatographic tank used

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(d) if the paper fits tightly.	For smooth and fast filtration process a gentle suction is developed. It is done by tight fitting of the filter paper in the glass funnel
(ii)	(b) is cooled at moderate rate to get medium sized crystals	• The hot filtered solution is then cooled at a moderate rate so that medium sized crystals are formed • Slow cooling yields bigger crystals which are likely to include considerable amount of solvent carrying impurities with it and complicating the drying process
(iii)	(c) distribution law	According to distribution law "A solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added." This law is applicable in solvent extraction as well as in chromatography
(iv)	(d) volatile or thermally unstable.	Since no heat is required during solvent extraction so no chances for decomposition of a sensitive compound.
(v)	(b) R_f value of solute	"It is the mathematical ratio which is obtained by dividing distance travelled by a component from original spot and the distance travelled by the solvent from original spot." $R_f = \frac{\text{Distance travelled by a component from the original spot}}{\text{Distance travelled by solvent from the original spot}}$

Q2. Fill in the blanks

(i) A complete chemical characterization of a compound must include ________.

(ii) During filtration the tip of stem of funnel should touch the side of beaker to avoid ________.

(iii) A fluted filter paper is used to ________ the process of filtration.

(iv) A solvent used for crystallization is required to dissolve ________ of the substance at its boiling point and ________ at room temperature.

(v) Repeated solvent extractions using small portions of solvent are ________ than using single extraction with larger volume of solvent.

ANSWERS

(i) both qualitative and quantitative analyses	(iv) large amount, small amount
(ii) splashing	(v) more efficient
(iii) increase / speed up	

Q.3 Tick the correct sentences. If the sentence is incorrect, write the correct statements.

(i) A qualitative analysis involves the identification of elements present in a compound.

(ii) If the process of filtration is to run smoothly, the stem of the funnel should remain empty.

(iii) If none of the solvents is found suitable for crystallization, a combination of two or more immiscible solvents may be used.

(iv) A solute distributes itself between two immiscible liquids in a constant ratio of concentrations depending upon the amount of solvent added.

(v) Paper chromatography is a technique of partition chromatography

ANSWERS

(i) True	(ii) False	(iii) False	(iv) False	(v) True

SHORT ANSWERS TO EXERCISE

Q10. You have been provided with a mixture of three inks with different colours. Write down a procedure to separate the mixture by paper chromatography.

Ans. Apparatus and Chemicals

Strip of Whatmann's chromatographic paper No.1, capillary tubes, mixture of inks, mixture of suitable solvents, chromatographic tank. Sample of inks for references

Procedure

(i) Draw a line on strip close to its one end by a lead pencil

(ii) Now spot the line with mixture of inks and separate samples A, B, C inks with capillary tubes.

(iii) After drying, put it in chromatographic tank having solvent.

(iv) When solvent (along with spots) covers ¾th of strip, put it out and dry.

(v) Calculate the R_f values of each ink by noting distances covered by inks and solvent front.

(vi) Compare the R_f of spots in mixture with samples to evaluate the conclusion

$R_f = \frac{\text{Distance covered by ink from original spot}}{\text{Discover covered by solvent from original spot (Y)}}$

R_f of ink A $= \frac{A}{Y}$

R_f of ink B $= \frac{B}{Y}$

R_f of ink C $= \frac{C}{Y}$

Conclusion

Mixture contains three inks which are separated on the basis of their R_f values.

Additional Questions

Q. Is partition chromatography a modified form of solvent extraction? If yes, justify the statement.

Ans. Partition chromatography is a modified form of solvent extraction. In solvent extraction, extraction is done on the basis of relative affinity (distribution) of solute with the two immiscible solvents. This is explained by distribution co-efficient (K).

$$K = \frac{\text{Concentration of solute in organic phase}}{\text{Concentration of solute in aqueous phase}}$$

In partition chromatography, the process is done on the basis of relative affinity of solute with the two phases i.e. stationary and mobile phase. This is also explained by distribution co-efficient (K)

$$K = \frac{\text{Concentration of a component in the moving phase}}{\text{Concentration of that component in the stationary phase}}$$

Q. Hot saturated solution is cooled at moderate rate during crystallization. Why?

Ans. When hot saturated solution is cooled at moderate rate, medium sized crystals are obtained. Due to

which these crystals have following advantages

(i) Crystals are less likely to include impurities, hence, are pure

(ii) Crystals are less likely to include solvent, hence are easy to dry.

Whereas slow cooling produces bigger sized crystals which represents opposite to above advantages and rapid cooling leads to improper crystallization

Q. What are factors that decide solvent extraction or crystallization, a technique selected for purification of a compound?

Ans. When crude product to be purified is volatile or thermally unstable, then solvent extraction is used as purification technique because no heating is required in this technique. Crystallization cannot be done because heating is required to form saturated solution. Heat can evaporate the volatile compound or can decompose thermally unstable compound Whereas in case of non-volatile or thermally stable compound, crystallization is done

Q. Differentiate between residue and filtrate.

Ans.

Residue	Filtrate
The insoluble particles which are left behind on the filter paper after the filtration is called as residue.	The clear liquid which is obtained in beaker after the filtration is called as filtrate.
Residue is either consists of insoluble impurities, precipitates or crystals.	Filtrate is either a pure solvent or a solution separated from impurities.

Q. What are the requirements for a smooth filtering process?

Ans. If the process of filtration is to run smoothly, we should observe following points.

(i) The filter paper should be large enough so that it is ¼ to ⅓ full of precipitates at the end of filtration.

(ii) The funnel should, in turn be large enough from its rim to extend 1-2 cm above the top circumference of the paper.

(iii) The stem of the funnel should remain continuously full of liquid.

(iv) The stem of the funnel should be several inches long so that it can extend a few cm into the beaker

(v) It should touch the side of the beaker to avoid splashing.

Previous Board Questions

Q. How desiccator is used for drying the crystal?

Q. What is distribution coefficient? To which technique it is applicable?

Q. Define distribution law and how it is helpful in solvent extraction.

Q. Why should tip of funnel be touched with the wall of beaker during filtration?

For Answers study Scholar's CHEMISTRY (Objective) XI

Chapter 3

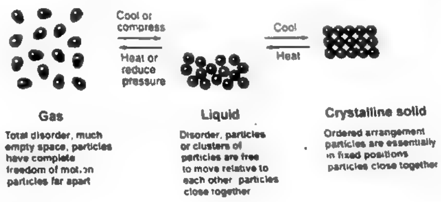
GASES

STATES OF MATTER

Matter exists in the following four states

(i) Gas **(ii)** Liquid **(iii)** Solid **(iv)** Plasma

- The simplest form of matter is the gaseous state
- The most of matter around us (on earth) is in the solid state
- Liquids are less common than solids, gases and plasmas because they can exist only within a relatively narrow range of temperature and pressure



Properties of Gases

(i) Shape

Gases do not have a definite shape. They take the shape of the container in which they are placed

(ii) Volume

There is no significant attractive force in the gas molecules and therefore the gases fill the whole space available to them. Hence, their volume becomes equal to the volume of the container in which they are placed

(iii) Low Density

Due to large empty spaces in between the gas molecules, the gases occupy a higher volume. Hence, the gases will have a low density (d = m/v). Due to this reason, the gases bubble up through the liquids and tend to rise

(iv) Diffusion

Two or more gases intermix readily to form a homogeneous mixture. This is called diffusion of gases. Diffusion is due to collision of gas molecules.

(v) Effusion

Gas molecules can pass through an extremely small hole from a region of higher pressure to a region of lower pressure. This is known as effusion of gases

(vi) Compressibility

Due to large empty spaces in between the gas molecules the gases [illegible] application of pressure

(vii) Expansibility

When the pressure on a gas is reduced, the gas molecules move away from one another. Hence, the volume of the gas is increased or in other words the gas expands. The gas also expands on heating.

(viii) Cooling by Expansion

When a highly compressed gas is allowed to expand suddenly, it produces cooling. This phenomenon is called Joule-Thomson effect.

(ix) Gases Exert Pressure

The gas molecules are in the state of constant rapid and random motion. Due to this motion, the gas molecules collide with the walls of the container. These collisions on the walls of the container cause pressure.

(x) Intermolecular Forces

The intermolecular forces in gases are very weak.

Properties of Liquids

(i) Volume

Liquids have a fixed volume. The intermolecular forces in liquids are strong enough to maintain a fixed volume.

(ii) Shape

Liquids do not have a fixed shape. They always take the shape of the container in which they are placed. The intermolecular forces are present in liquids but they are not so strong that a liquid can have a fixed shape.

(iii) Evaporation

Due to constant movement and collisions between the liquid molecules, the high energy molecules leave the surface of liquid and the liquid is changed into its vapours. This process is called evaporation. Liquids evaporate at all temperatures.

(iv) Diffusion

A liquid can diffuse into another liquid with which it is miscible. However, the rate of diffusion in liquids is slower than in gases. This is due to less empty spaces between the liquid molecules.

(v) High Density

Due to smaller intermolecular distances, the liquids occupy less volume. Hence, the liquids will have a higher density ($d = m/v$) than gases.

(vi) Intermolecular Distance

The intermolecular distance in liquids is negligible just like solids.

(vii) Intermolecular Forces

The intermolecular attractive forces in liquids are intermediate between gases and solids. The melting and boiling points of gases, liquids and solids depend upon the strength of such forces.

(viii) Solidification

Molecules of liquids possess kinetic energy due to their motion. Liquids can be converted into solids on cooling i.e., by decreasing their kinetic energy. Molecules of liquids collide among themselves and exchange energy but those of solids cannot do so.

Properties of Solids

(i) Shape and Volume

Solids have a definite shape and volume due to strong intermolecular forces.

(ii) Non-Compressibility

The particles present in a solid are already very close to one another. These particles are very tightly packed and the empty spaces in between them are extremely small. Hence, solids cannot be further compressed.

(iii) Diffusion

Due to close packing and fixed position of the particles, one solid cannot diffuse into the other.

(iv) Movement of particles

There is only vibratory motion in the solid particles.

PRESSURE

"Force per unit area is called pressure."

$$P = \frac{F}{A}$$

Units of Pressure

(i) Atmosphere

"The pressure of air that can support 760 mm or 76 cm Hg column at sea level at 0°C is called one atmosphere."

or

"The force exerted by 760 mm or 76 cm Hg column on an area of 1 cm^2 at sea level at 0°C is called one atmosphere."

$$1\ atm = 760\ mm\ Hg = 76\ cm\ Hg$$

- A penny sitting on the tip of your finger exerts a pressure of about 250 Pa

(ii) Nm^{-2} - SI Unit of Pressure

In SI system of units

$$P = \frac{N}{m^2}$$

$$P = Nm^{-2}$$

The first scientist to study pressure was "Blaise Pascal" so the unit of pressure is also named after him.

$$1\ Pascal = 1\ Nm^{-2}$$

$$1\ Pa = 1\ Nm^{-2}$$

Also $1\ atm = 101325\ Nm^{-2}$

As $1\ Nm^{-2} = 1\ Pa$

So $1\ atm = 101325\ Pa = 101.325$ kilopascals

One millimeter of mercury, also called "a torr" after an Italian scientist **Evangelista Torricelli** is based on atmospheric pressure measurements using a barometer.

(iii) torr (used in scientific work)

$$1\ torr = 1\ mm\ Hg$$

$$760\ torr = 760\ mm\ Hg$$

$$1\ atm = 760\ torr = 101325\ Nm^{-2}$$

(iv) Pound Per Square Inch (psi) (used in engineering work)

$$1\ atm = 14.7\ psi$$

(v) Millibar (used by meteorologist):

$$1\ atm = 1013.25\ millibar$$

$$1\ atm = 1.01325\ bar$$

Relationship between pressure units:

$$1\ atm = 14.7\ psi = 760\ torr = 101325\ Nm^{-2} = 101.325\ kPa = 1.01325\ bar$$

- **Boyle's Law** ($V \propto \frac{1}{P}$ at constant temperature.)
- **Charles's Law** ($V \propto T$ at constant pressure.)
- **Dalton's Law of partial pressure** ($P_t = P_1 + P_2 + P_3 + \ldots P_n$)
- **Graham's Law of diffusion** $\left(\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}\right)$

GAS LAWS

"The relationships between volume of a given amount of gas and the prevailing conditions of temperature and pressure are called the gas laws."

BOYLE'S LAW

Statement

"The volume of a given mass of a gas at constant temperature is inversely proportional to the pressure applied to the gas."

Mathematically

$V \propto \frac{1}{P}$ (at constant temperature and number of moles)

$V = \frac{k}{P}$ Here 'k' is proportionality constant

$PV = k$ (when 'T' and 'n' are constant)

The value of k is different for the different amounts of the same gas.

Another Statement

"The product of pressure and volume of a fixed amount of a gas at constant temperature is a constant quantity."

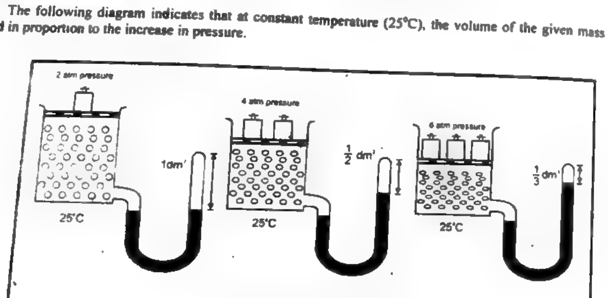
So, $P_1V_1 = k$ and $P_2V_2 = k$

Hence, $P_1V_1 = P_2V_2$

P_1V_1 are the initial values of pressure and volume while P_2V_2 are the final values of pressure and volume

Experimental Verification

The following diagram indicates that at constant temperature (25°C), the volume of the given mass of a gas is reduced in proportion to the increase in pressure.



Verification of Boyle's Law

Let us take a gas cylinder having a moveable piston. The cylinder is also attached with a manometer to read the pressure of the gas directly. Let the initial volume of gas is $1dm^3$ and its pressure is 2 atmospheres when the piston has one weight on it. When the piston is pressed twice with the help of two equal weights, the pressure becomes four atmospheres. Similarly, when the piston is loaded with a mass three times greater, then the pressure becomes six atmospheres. The initial volume of the gas at two atmospheres is $1dm^3$, it is reduced to $\frac{1}{2}dm^3$ and then $\frac{1}{3}dm^3$ with increase of weights, respectively

$P_1V_1 = 2\ atm \times 1\ dm^3 = 2\ dm^3\ atm = k$

$P_2V_2 = 4\ atm \times \frac{1}{2}\ dm^3 = 2\ dm^3 atm = k$

$P_3V_3 = 6\ atm \times \frac{1}{3}\ dm^3 = 2\ dm^3 atm = k$

Hence, Boyle's law is verified.

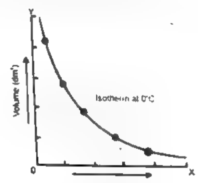
The value of k will remain the same for the same quantity of a gas at the same temperature.

Graphical Explanation of Boyle's Law

Graph # 1

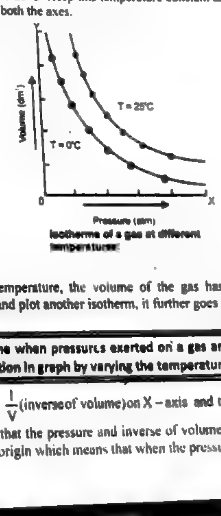
Q4b. What are isotherms? What happens to the positions of isotherms when they are plotted at high temperature for a particular gas?

Let us take a particular amount of a gas at 0°C temperature. When the pressure of the gas is changed, volume also changes. Increase in pressure decreases the volume. If a graph is plotted between pressure on the x-axis (abscissa) and volume on the y-axis (ordinate) at a constant temperature, then a curve is obtained. This curve is called isotherm 'iso' means same, "therm" means heat.



Isotherm of gas at 0 °C.

Now increase the temperature of the gas to 25°C. Keep this temperature constant and again vary the pressure and volume, and plot the isotherm. It goes away from both the axes.



Isotherms of a gas at different temperatures

Reason

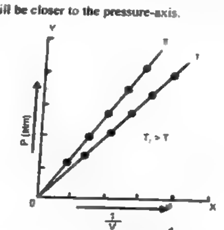
The reason is that at high temperature, the volume of the gas has increased. Similarly, if we increase the temperature further, make it constant and plot another isotherm, it further goes away from the axes.

Graph#2

Q4c. Why do we get a straight line when pressures exerted on a gas are plotted against inverse of volume? This straight line changes its position in graph by varying the temperature? Justify it.

If a graph is plotted between $\frac{1}{V}$ (inverse of volume) on X – axis and the pressure P on the Y – axis then a straight line is obtained. This shows that the pressure and inverse of volume are directly proportional to each other. This straight line will meet at the origin which means that when the pressure is very close to zero, then the volume is so

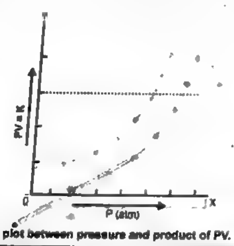
high that its inverse is very close to zero. By increasing the temperature of the same gas from T_1 to T_2 and keeping it constant, one can vary pressure and volume. The graph of this data between P and $\frac{1}{V}$ will give another straight line. This straight line at T_2 will be closer to the pressure-axis.



A plot between p and $\frac{1}{V}$

Graph # 3

If we plot a graph between pressure on X-axis and the product PV on Y-axis, a straight line parallel to the pressure axis is obtained. This straight line indicates that 'k' is a constant quantity. At higher constant temperature, the volume increases and value of product PV should increase due to increase of volume at same pressure, but PV remains constant at this new temperature and a straight line parallel to the pressure axis is obtained. This type of straight line will help us to understand the non-ideal behaviour of gases. Boyle's law is applicable only to ideal gases.



A plot between pressure and product of PV.

Q. (a) How will you explain that value of constant k in the equation PV = k depends upon

(i) Temperature of the gas

(ii) Quantity of the gas

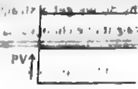
Ans. According to Boyle's law:

$V \propto \frac{1}{P}$ or

PV = k (if quantity of gas 'n' and temperature 'T' is kept constant)

If we plot a graph between P and PV for a fixed quantity of a gas at constant temperature we obtain a straight line parallel to x-axis, indicating that

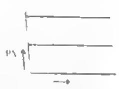
PV = k



By changing the 'n' or 'T' of a gas, volume of gas is changed so a change occurs in graph

(i) At higher constant temperature, volume increase and the product 'PV' increases. Another line parallel to X-axis is obtained which is higher than initial line and vice versa

(ii) With the greater value of 'n' volume will be increased, which results in an increase of 'PV' value. So a new horizontal line is obtained, higher than the original line



Q15. Explain the following facts:

(i) The plot of PV versus P is a straight line at constant temperature and with a fixed number of moles of an ideal gas

Ans. According to Boyle's law

$V \propto \frac{1}{P}$ (when the temperature and number of moles are constant)

or PV = k

If a graph is plotted between product PV on Y-axis and pressure on X-axis for a fixed quantity of a gas at constant temperature, then a straight line parallel to X-axis is obtained. This straight line indicates that 'k' is a constant quantity under all conditions of temperature and pressure for an ideal gas

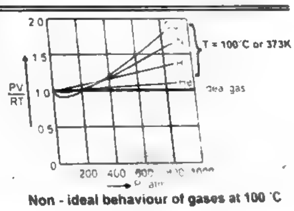

A plot between pressure and product of PV

(ii) The straight line obtained when product PV is plotted against P is parallel to the pressure axis and goes away from the pressure axis at high pressures for many gases.

Ans. When PV is plotted against P for a fixed quantity of an ideal gas at a constant temperature, a straight line parallel to x-axis is obtained

For many real gases the straight line goes away from pressure axis at higher pressures

The reason is that when pressure increases, molecules come close to each other and intermolecular forces increase. In this way real gases do not remain ideal.



Non - ideal behaviour of gases at 100 °C

CHARLES'S LAW

It is a quantitative relationship between temperature and volume of a gas and was given by French scientist J. Charles in 1787.

Statement

"The volume of the given mass of a gas is directly proportional to the absolute temperature at constant pressure."

Mathematically

$V \propto T$ (at constant pressure and number of moles)

or $V = kT$

or $\frac{V}{T} = k$

Absolute Temperature.
The temperature measured in Kelvin scale called absolute temperature

Q. Which of the following is absolute temperature?
(a) 273.16 t
(b) 100°t
(c) 9Xk
(d) all of these

If temperature is changed from T_1 to T_2, and volume changes from V_1 to V_2, then

$$\frac{V_1}{T_1} = k \quad \text{and} \quad \frac{V_2}{T_2} = k$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

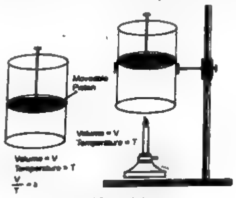
Another Statement

"The ratio of volume to temperature remains constant for same amount of gas at same pressure."

Experimental Verification

Let us consider a certain amount of a gas enclosed in a cylinder fitted with a moveable piston.

The volume of the gas is V_1 and its temperature is T_1. When the gas in the cylinder is heated, both volume and temperature of the gas increase. The new values of volume and temperature are V_2 and T_2 respectively.



Verification of Charles's Law

Result

The experiment shows that:

$$\frac{V_1}{T_1} = k \quad \text{and} \quad \frac{V_2}{T_2} = k$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Hence, Charles's law is verified.

Derivation of Absolute Zero

Absolute Zero

"The hypothetical temperature at which the volume of a gas is supposed to become zero if the gas remains in gaseous state."

$$0K = -273.16°C = -459°F$$

Quantitative Definition of Charles's Law

"At constant pressure, the volume of the given mass of a gas increases or decreases by 1/273 of its original volume at 0°C for every 1°C rise or fall in temperature respectively."

General equation for volume of gas

The general equation to know the volumes of the gas at various temperatures is:

$$V_t = V_o\left(1 + \frac{t}{273}\right)$$

Where V_t = Volume of gas at temperature T
V_o = Volume of gas at 0°C.
t = Temperature on centigrade or Celsius scale.

Explanation

If a gas is warmed by 1°C, it expands by 1/273 of its original volume at 0°C. Since, original volume is 546 cm^3, so for 1°C rise in temperature, 2 cm^3 increase in volume will take place.

2 cm^3 is the 1/273 of 546 cm^3. Similarly for 100°C rise in temperature, a change of 200 cm^3 will take place

Volume-Temperature data for a given amount of a gas at constant pressure

Volumes (cm^3)	Celsius Temperature (°C)	Temperature (K)	$\frac{V}{T} = k = cm^3K^{-1}$
1092	273	546	2
846	150	423	2
746	100	373	2
646	50	323	2
566	10	283	2
548	1	274	2
546	0	273	2
544	−1	272	2
526	−10	263	2
400	−73	200	2
346	−100	173	2
146	−200	73	2
0	−273	0	

Conclusions

(i) The above table shows that at 0°C, the volume of the gas taken is 546 cm^3. It is twice 273 cm^3, and is being supposed for the sake of convenience of understanding. At 273°C, the volume of the gas has doubled (1092 cm^3) and it should become practically zero at −273°C.

(ii) The volume does not increase corresponding to increase in temperature on Celsius scale. e.g. the increase in temperature from 10°C to 100°C increases the volume from 566cm^3 to 746cm^3.

Applications of Charles's Law

By using Celsius Scale

Applying Charles's law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{566}{10} \neq \frac{746}{100}$$

The two sides of equation are not equal. So, Charles's law is not being obeyed when temperature is measured on the Celsius scale.

By using Kelvin Scale

Charles's law is obeyed when the temperature is taken on the Kelvin scale. For example, at 283 K (10°C), the volume is 566 cm^3, while at 373 K (100°C), the volume is 746 cm^3.

According to Charles's law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = k$$

$$\frac{566}{283} = \frac{746}{373} = 2 = k$$

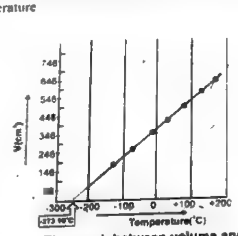
So Kelvin scale was developed to verify Charles's law

Graphical Explanation of Charles's Law

If we plot a graph between temperature on x-axis and the volume of one mole of an ideal gas on y-axis, we get a straight line which cuts the temperature axis at −273 16°C

Lowest possible temperature

This can by possible only if we extrapolate the graph upto −273.16°C. This temperature is the lowest possible temperature, which would have been achieved if the substance remains in the gaseous state. Actually, all the gases are converted into liquids above this temperature



The graph between volume and temperature for a gas.

Effect of mass on slope

Greater the mass of gas taken, greater will be the slope of straight line. The reason is that greater the number of moles, greater the volume occupied. All these straight lines when extrapolated meet at a single point of −273.16°C (0K).

Behaviour of a real gas

It is apparent that this temperature of −273.16°C will be attained when the volume becomes zero. But for a real gas, the zero volume is impossible which shows that this temperature cannot be attained for a real gas. This is how we recognize that −273 16°C must represent the coldest temperature.

Q5c. Do you think that the volume of any quantity of a gas become zero at −273.16°C? Is it not against the law of conservation of mass? Deduce idea of Absolute zero from this discussion.

Ans. **Law of conservation of mass is stated as**

"Mass can neither be created nor be destroyed although it can change from one form to another."

If a gas could have a zero volume at −273.16°C, then its mass will also become equal to zero which is against the law of conservation of mass.

So the volume of any quantity of gas is never equal to zero at −273.16°C. All real gases liquefy before reaching this temperature

Absolute Zero:

"A hypothetical temperature (−273.16°C) where volume of a given mass of gas practically becomes equal to zero is called absolute zero."

It is unattainable. Absolute zero (−273.16°C) is a theoretical value.

Q5b. Throw some light on the factor 1/273 in Charles's law.

Ans. The factor 1/273 is introduced in mathematical form of quantitative definition of Charles's law.

The equation is

$$V_t = V_o\left(1 + \frac{t}{273}\right)$$

where V_t = volume of gas at any temperature

V_o = volume of gas at 0°C

t = temperature of gas

The equation shows that if V_o is known for a gas then an increase or decrease in temperature by 1°C results in an increase or decrease of its volume by a factor 1/273. According to the factor 1/273, the V_t of a gas should become $2V_o$ at 273°C (doubles) and zero at −273°C

Importance:

So factor 1/273 is very important to explain Charles's law and helpful in evaluation of absolute scale

THERMOMETRY

"The art of measuring temperature of substances is called thermometry."

Scales of Thermometry

The following three scales are used for temperature measurements

(I) Centigrade Scale or Celsius Scale

It has a zero mark (0°C) for the temperature of ice at one atmospheric pressure. The mark 100°C indicates the temperature of boiling water at one atmospheric pressure. The space between these temperature marks is divided into 100 equal parts and each part is 1°C

(II) Fahrenheit Scale

The melting point of ice at 1 atmospheric pressure has a mark 32°F and that of boiling water is 212°F. The space between these temperature marks is divided into 180 equal parts and each part is 1°F.

(III) Kelvin Scale or Absolute Scale

The melting point of ice at 1 atmospheric pressure is 273 K. The water boils at 373 K or more precisely at 373.16 K.

Interconversion of Temperature Scales

- The following relationships help us to understand the interconversion of various scales of temperature.

°C to K: K = °C + 273.16

°F to °C: °C = 5/9(°F − 32)

°C to °F: °F = 9/5(°C) + 32

> −40°C is the temperature which is common in Celsius and Fahrenheit scales.

GENERAL GAS EQUATION

Q7a. What is the general gas equation? Derive it in various forms?

- According to Boyle's law:

$$V \propto \frac{1}{P} \quad \text{(when n and T are constant)}$$

- According to Charles's law:

$$V \propto T \quad \text{(when n and P are constant)}$$

- According to Avogadro's law:

$$V \propto n \quad \text{(when P and T are constant)}$$

If we think for a moment that none of the variables are to be kept constant, then all the above three relationships can be joined together as follows:

$$V \propto \frac{nT}{P}$$

> If the pressure is written as force per unit area and volume as area times length,
> R = [illegible]
> $= \frac{\text{force} \times \text{length}}{n \times T}$
> $= \frac{\text{work}}{nT}$
> Hence R can be expressed in units of work or energy per degree per mole.

$$V = \text{constant}\,\frac{nT}{P}$$

General gas constant

The constant suggested is R which is called general gas constant.

$$V = R\frac{nT}{P}$$

$$PV = nRT$$

This is called an ideal gas equation or general gas equation. This equation shows that if we have any quantity of an ideal gas then the product of its pressure and volume is equal to the product of number of moles, general gas constant and absolute temperature.

Derivation of Gas Laws from General Gas Equation

The following gas laws can be derived from general gas equation:

Boyle's law

$PV = nRT$ (when T and n are constant)

$PV = k$

Charles's law

$V = R\frac{nT}{P}$ (when P and n are constant)

$V = kT$

Avogadro's law

$V = R\frac{nT}{P}$ (when P and T are constant)

$V = kn$

For one mole of a gas

For one mole of a gas, the general gas equation is:

$n = 1$

$PV = RT$ or $\frac{PV}{T} = R$

It means that ratio of PV to T is a constant quantity (molar gas constant).

Hence,

$$\frac{P_1V_1}{T_1} = R \qquad \frac{P_2V_2}{T_2} = R$$

Therefore,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This is another form of general gas equation.

Standard pressure:
$1atm = 760\ torr = 101325 Nm^{-2}$
Standard temperature:
273.16K
Molar volume:
$22.414 dm^3 = 22414 cm^3 = 0.022414 m^3$

IDEAL GAS CONSTANT (R)

Q8. Derive units for gas constant 'R' in general gas equation

(a) When Pressure is in atm and Volume in dm^3

(b) When Pressure is in Nm^{-2} Volume in m^3

(c) When energy is expressed in ergs

Values and Units of R

- **Avogadro's principle** is used to calculate values and units of R. According to this principle "The volume of one mole of an ideal gas at STP (one atmospheric pressure and 273.16 K) is 22.414 dm^3."

- Its value depends upon the units chosen for **pressure, volume and temperature.**
- **General gas equation** is used to calculate the value of R

To evaluate 'R', the general gas equation can be written as

$$PV = nRT$$

$$R = \frac{PV}{nT}$$

Q. The value and units of "R" depends upon
(a) pressure of gas
(b) temperature of gas
(c) volume of gas
(d) units used for pressure and volume

(a) When P in atm and V in dm^3

$P = 1$ atm $\quad n = 1$ mole

$V = 22.414\ dm^3 \quad T = 273.16$ K

$$R = \frac{PV}{nT} = \frac{1atm \times 22.414 dm^3}{1mol \times 273.16K}$$

$$R = 0.0821\ atm\ dm^3 mol^{-1} K^{-1}$$

Physical meanings of value of R

The physical meanings of this value is that, if we have one mole of an ideal gas at 273.16 K and one atmospheric pressure and its temperature is increased by 1 K, then it will absorb 0.0821 dm^3 atm of energy. dm^3 atm is the unit of energy in this situation. Hence, the value of R is a universal parameter for all the gases. It tells us that the Avogadro's number of molecules of all the ideal gases have the same demand of energy.

(b) When P in torr or mmHg and V in dm^3

$P = 760$ torr $\quad n = 1$ mole

$V = 22.414\ dm^3 \quad T = 273.16$ K

$$R = \frac{PV}{nT} = \frac{760 torr \times 22.414 dm^3}{1mol \times 273.16K}$$

$$R = 62.4 dm^3\ torr\ or\ mmHg\ mol^{-1} K^{-1}$$

(c) When P in torr or mmHg and V in cm^3

$P = 760$ torr $\quad n = 1$ mole

$V = 22414\ cm^3 \quad T = 273.16$ K

$$R = \frac{PV}{nT} = \frac{760 torr \times 22414 cm^3}{1mol \times 273.16K}$$

$$R = 62400 cm^3\ torr\ or\ mmHg\ mol^{-1} K^{-1}$$

(d) Value and Units of R in SI

The SI units of pressure are Nm^{-2} and of volume are m^3. By using Avogadro's principle.

$n = 1$ mol $\quad T = 273.16$ K

$V = 22.414\ dm^3 = 0.022414\ m^3$

$P = 1$ atm $= 101325\ Nm^{-2}$

$$R = \frac{PV}{nT} = \frac{101325 Nm^{-2} \times 0.022414 m^3}{1mol \times 273.16K}$$

$$R = 8.3143\ Nm\ K^{-1} mol^{-1} = 8.3143\ JK^{-1} mol^{-1}\ (1Nm = 1J)$$

Keep in mind that, wherever the pressure is given in Nm^{-2} and the volume in m^3, then the value of R used must be $8.3143 JK^{-1} mol^{-1}$.

(e) Since $1cal = 4.18$ J

So, $R = \frac{8.3143}{4.18} = 1.987 cal K^{-1} mol^{-1}$

(f) **When energy is expressed in ergs**

Since $1J = 10^7$ erg

So, $R = 8.3143\ J.mol^{-1}K^{-1}$

$R = 8.3143 \times 10^7 ergs\,mol^{-1}K^{-1}$

Applications of the General Gas Equation

The general gas equation can be used to calculate the molecular mass, density and mass of the gas

(i) Calculation of the Density of a Gas

The general gas equation is

$$PV = nRT$$

n = Number of moles of the gas

$$n = \frac{\text{mass of the gas in g}}{\text{molar mass of the gas}} = \frac{m}{M}$$

Hence, $PV = \frac{m}{M}RT$

$$PM = \frac{m}{V}RT$$

$$PM = dRT \qquad \left[d = \frac{\text{mass}}{\text{Volume}}\right]$$

$$d = \frac{PM}{RT}$$

Hence, the density of the gas can be calculated with the help of this equation.

(ii) Calculation of the Molecular Mass of a Gas

The general gas equation is:

$$PV = nRT$$

Where n is equal to number of moles of the gas

$$n = \frac{\text{mass of the gas in g}}{\text{molar mass of the gas}} = \frac{m}{M}$$

Now put the value of n in the gas equation

$$PV = \frac{m}{M}RT$$

$$PM = \frac{m}{V}RT$$

$$PM = dRT \left[d = \frac{\text{mass}}{\text{Volume}}\right]$$

$$M = \frac{dRT}{P}$$

Hence, the molecular mass of a gas can be calculated with the help of this equation.

(iii) Calculation of the Mass of a Gas

We know that the density of the gas can be calculated with the help of following formula:

$$d = \frac{PM}{RT}$$

$$\frac{m}{V} = \frac{PM}{RT}$$

$$m = \frac{PMV}{RT}$$

Q7b. Can we determine the molecular mass of an unknown gas if we know the pressure, temperature and volume along with the mass of that gas?

Ans. We can determine the molecular mass as follows

Derivation:

$PV = nRT$ (general gas equation)

where $n = \frac{\text{mass of gas}}{\text{molecular mass}} = \frac{m}{M}$

So $PV = \frac{m}{M}RT$

$$M = \frac{m}{V \times P}RT$$

So by knowing m, V, P, T for a gas, one can determine its molecular mass.

Q7c. How do you justify from general gas equation that increase in temperature or decrease in pressure decreases the density of a gas?

Ans.

$PV = nRT$

where $n = \frac{m}{M}$

$PV = \frac{m}{M}RT$

$PM = \frac{m}{V}RT$ where $\frac{m}{V} = d$

$PM = dRT$

$d = \frac{PM}{RT}$

for a gas M and R are constants

so $d \propto P$

and $d \propto \frac{1}{T}$

So density of a gas increases with increase in pressure and decrease with an increase in temperature

$PV = nRT$
$n = \frac{m}{M}$
$PV = \frac{m}{M}RT$
$PM = \frac{m}{V}RT$ ∴ $\frac{m}{V} = d$
$PM = dRT$
$d = \frac{PM}{RT}$
for a gas M and R are
$d \propto P$ & $d \propto \frac{1}{T}$

Q7d. Why do we feel comfortable in expressing the densities of gases in units of g dm^{-3} rather than g cm^{-3}, a unit which is used to express the densities of liquids and solids.

Ans. In gases, particles are very far away from each other as compared to solids and liquids. So appreciable mass of a gas is not present in a smaller volume i.e., 1 cm^3. Therefore, density of gases is expressed in a bigger unit of volume i.e., g dm^{-3} instead of g cm^{-3}.

Example. CH_4 gas has a density 0.7138 g dm^{-3} at 0°C. If we express it in g cm^{-3}, it would be 0.0007138 g cm^{-3} which is a very small value.

Thus units of density of gases are:

g dm^{-3} (commonly used)

kg m^{-3} (SI unit)

AVOGADRO'S LAW

Statement

"Equal volumes of all the ideal gases at the same temperature and pressure contain equal number of molecules."

Explanation

Since, one mole of an ideal gas at 273.16 K and one atmospheric pressure (STP) has a volume of 22.414 dm^3 and one mole of a gas has Avogadro's number of molecules. So, 22.414 dm^3 of ideal gas at STP will have Avogadro's number of molecules i.e., 6.02×10^{23} molecules.

Examples

i) $H_2 = 2\ g = 1$ mole $= 22.414\ dm^3$ at STP $= 6.02 \times 10^{23}$ molecules
ii) $O_2 = 32\ g = 1$ mole $= 22.414\ dm^3$ at STP $= 6.02 \times 10^{23}$ molecules
iii) $N_2 = 28\ g = 1$ mole $= 22.414\ dm^3$ at STP $= 6.02 \times 10^{23}$ molecules
iv) $CH_4 = 16\ g = 1$ mole $= 22.414\ dm^3$ at STP $= 6.02 \times 10^{23}$ molecules

So, one mole of all gases at STP will have same volume of $22.414\ dm^3$ and same number of molecules i.e., 6.02×10^{23} but their masses are not equal. Similarly if we have one dm^3 of H_2, O_2, N_2 and CH_4 in separate vessels at STP, then they have same number of molecules i.e., 2.68×10^{22} molecules.

No doubt, one dm^3 of H_2 at STP weighs approximately 0.0899 grams and one dm^3 of O_2 at STP weighs 1.4384g, but their number of molecules are the same. Although, oxygen molecule is 16 times heavier than hydrogen, but this does not disturb the volume occupied, because molecules of the gases are widely separated from each other at STP. One molecule is approximately at a distance of 300 times its own diameter from its neighbor at room temperature.

Applications of Avogadro's Law:

- Determination of atomicity of elementary gases.Atomicity is the number of atoms present in a molecule.
- To show that, 2 x Vapour density = Molecular mass.
- Vapour density of a gas is the ratio of the mass of certain volume of gas to the mass of the same volume of hydrogen at the same temperature and pressure.
- To show that Molar volume (Gram molecular volume) of all gases is the same at STP.
- The Molar volume (gram molecular volume) of a gas is the volume occupied by one mole of gas at standard temperature and pressure and is 22.4 litres or $22{,}400\ cm^3$.
- One mole of all gases at STP will occupy 22.4 litres.

Q9b. Do you think that 1 mole of H_2 and 1 mole of NH_3 at 0°C and 1 atm pressure will have Avogadro's number of particles?

Ans. According to Avogadro's law

"Equal volumes of all the ideal gases at the same temperature and pressure contain equal number of molecules."

1 mole of H_2 and 1 mole of NH_3 occupy $22.414\ dm^3$ at 0°C and 1 atm pressure separately.

Since both gases occupy same volume. So according to Avogadro's law they will have same number of particles i.e., 6.02×10^{23} molecules

1 mole of $H_2 = 22.414\ dm^3$ of $H_2 = 6.02 \times 10^{23}$ molecules of H_2

1 mole of $NH_3 = 22.414\ dm^3$ of $NH_3 = 6.02 \times 10^{23}$ molecules of NH_3

Q9c. Justify that $1\ cm^3$ of H_2 and $1\ cm^3$ of CH_4 at STP will have same number of molecules when one molecule of CH_4 is 8 times heavier than that of H_2?

Ans. According to Avogadro's law:

"Equal volumes of all the ideal gases at the same temperature and pressure contain equal number of molecules."

Since both gases have same volume i.e., $1\ cm^3$ ($0.001\ dm^3$) at STP so both contain equal number of molecules.

We can justify it mathematically

Data: Volume of H_2 gas $= 1\ cm^3 = 0.001\ dm^3$

Molar volume of H_2 gas $= 22.414\ dm^3$ at STP

Volume of CH_4 gas $= 1\ cm^3 = 0.001\ dm^3$

Molar volume of CH_4 gas $= 22.414\ dm^3$ at STP

Required: number of H_2 molecules = ?

number of CH_4 molecules = ?

Solution:

$$\text{Number of particles} = \frac{N_A \times \text{Volume of gas}}{\text{Molar volume}}$$

(i) $$\text{Number of } H_2 \text{ molecules} = \frac{6.02\times10^{23}\times0.001\ dm^3}{22.414\ dm^3}$$

Answer = 2.68×10^{19} molecules

(ii) $$\text{no. of } CH_4 \text{ molecules} = \frac{6.02\times10^{23}\times0.001\ dm^3}{22.414\ dm^3}$$

Answer = 2.68×10^{19} molecules

Although, methane molecule CH_4 is eight times heavier than hydrogen molecule H_2 but this does not disturb the volume occupied, because molecules of the gases are widely separated from each other at STP One molecule is approximately at a distance of 300 times its own diameter from its neighbour at room temperature

DALTON'S LAW OF PARTIAL PRESSURES

Statement

"The total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures."

Mathematical form

Let, the gases are designated as 1, 2 & 3 and their partial pressures are p_1, p_2 & p_3 respectively The total pressure P_t of the mixture of gases is given by:

$$P_t = p_1 + p_2 + p_3$$

Partial pressure

"The partial pressure of a gas in a mixture of gases is the pressure that it would exert on the walls of the container, if it were present in that same volume under the same temperature."

Explanation

Let us have four cylinders of same volume i.e. $10\ dm^3$ each and three gases hydrogen (H_2), methane (CH_4) and oxygen (O_2) are separately enclosed in first three of them at the same temperature.

Let, the partial pressures of H_2, CH_4 and O_2 be 400 torr, 500 torr and 100 torr respectively. All these gases are transferred to the fourth cylinder of capacity $10\ dm^3$ at the same temperature.

According to Dalton's law:

$$P_t = p_{H_2} + p_{CH_4} + p_{O_2}$$
$$= (400 + 500 + 100)\ \text{torr}$$
$$P_t = 1000\ \text{torr}$$

Independent behaviour of gases

These three non-reacting gases are behaving independently under the normal conditions. The rapidly moving molecules of each gas in a mixture have equal opportunities to collide with the walls of the container. Hence, each gas exerts a pressure independent of the pressure of other gases. The total pressure is the result of total number of collisions per unit area in a given time.

General gas equation for the individual gases

Molecules of each gas move independently, so the general gas equation (PV = nRT) can be applied to the individual gases in the gaseous mixture.

(i) For H_2 gas

$$p_{H_2}V = n_{H_2}RT$$

$$p_{H_2} = n_{H_2}\frac{RT}{V} \qquad p_{H_2} \propto n_{H_2} \left(\because \frac{RT}{V} \text{ is a constant factor}\right)$$

(ii) For CH_4 gas

$$p_{CH_4}V = n_{CH_4}RT$$

$p_{CH_4} = n_{CH_4}\frac{RT}{V}$ $\quad p_{CH_4} \propto n_{CH_4}$ ($\because \frac{RT}{V}$ is a constant factor)

(iii) For O_2 gas

$p_{O_2}V = n_{O_2}RT$

$p_{O_2} = n_{O_2}\frac{RT}{V}$ $\quad p_{O_2} \propto n_{O_2}$ ($\because \frac{RT}{V}$ is a constant factor)

Conclusion

All these gases have their own partial pressure. Since, volumes and the temperatures are the same, so their number of moles will be different and will be directly proportional to their partial pressures. Adding these three equations:

$P_t = p_{H_2} + p_{CH_4} + p_{O_2}$

$P_t = (n_{H_2} + n_{CH_4} + n_{O_2})\frac{RT}{V}$

$P_t = n_t\frac{RT}{V}$ $\quad (\because n_t = n_{H_2} + n_{CH_4} + n_{O_2})$

$P_tV = n_tRT$

The total pressure of the mixture of gases depends upon the total number of moles of the gases

Calculation of Partial Pressure of a Gas

The partial pressure of any gas in a mixture of gases can be calculated, provided one knows

(i) Mass of the gas (number of moles)

(ii) Total pressure of the mixture

(iii) Total number of moles of the mixture

Derivation of equation

Suppose we have a mixture of gas A and gas B. This mixture is enclosed in a container having volume (V). The total pressure is 1 atm. The number of moles of the gases A and B are n_A and n_B respectively. If they are maintained at temperature T, then:

Equation for mixture of gases

$P_tV = n_tRT$ ...(i)

Equation for gas A:

$p_AV = n_ART$ ...(ii)

Equation for gas B:

$p_BV = n_BRT$ ...(iii)

Dividing eq. (ii) by (i):

$$\frac{p_AV}{P_tV} = \frac{n_ART}{n_tRT}$$

$$\frac{p_A}{P_t} = \frac{n_A}{n_t}$$

$$p_A = \frac{n_A}{n_t}P_t \quad ...(iv)$$

$p_A = X_AP_t$ $\quad$ (X_A is mole fraction of gas A)

Similarly $\quad p_B = X_BP_t$ $\quad$ (X_B is mole fraction of gas B)

Partial pressure of a gas is the mole fraction of that gas multiplied by the total pressure of the mixture. Remember that mole fraction of any one of the gases in the mixture is less than unity. Moreover, the sum of mole fraction is always equal to unity

Applications of Dalton's Law of Partial Pressures

Following are the four applications of Dalton's law of partial pressure

(i) Collection of gases over water

Some gases are collected over water in the laboratory. The gas during collection gathers water vapours and becomes moist. The pressure exerted by this moist gas is the sum of partial pressures of dry gas and that of water vapours. The partial pressure exerted by the water vapours is constant at a particular temperature and is called **aqueous tension**

$P_{moist} = p_{dry} + p_{w.vap}$

$P_{moist} = p_{dry}$ + aqueous tension

$p_{dry} = P_{moist}$ - aqueous tension

(ii) Process of respiration

The process of respiration depends upon the difference in partial pressures. When animals inhale air then oxygen moves into the lungs as the partial pressure of oxygen in the air is 159 torr, while the partial pressure of the oxygen in the lungs is 116 torr. CO_2 produced during respiration moves out in the opposite direction, as its partial pressure is more in the lungs than that in the air

(iii) Breathing at higher altitudes

At higher altitude, the pilot feels uncomfortable breathing because the partial pressure of oxygen in the un-pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing

(iv) Breathing in the depth of sea

Deep sea divers take oxygen mixed with an inert gas say He and adjust the partial pressure of oxygen according to the requirement. Actually, in sea after every 100 feet depth, the diver experiences approximately 3 atm pressure, so normal air cannot be breathed in depth of sea. Moreover, the pressure of N_2 increases in depth of sea and it diffuses in the blood.

Q108. Dalton's law of partial pressures is only obeyed by those gases which do not have attractive forces among their molecules? Justify it.

Ans. According to Dalton's law

"The total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures at a given temperature."

If the gases have attractive forces among their molecules, then the gases will not exert the same pressure which they would exert independently. So

$$P_t \neq p_1 + p_2 + p_3$$

and Dalton's law is not followed.

Therefore to obey Dalton's law, only those mixtures of gases are considered which have no attractive forces among them.

DIFFUSION

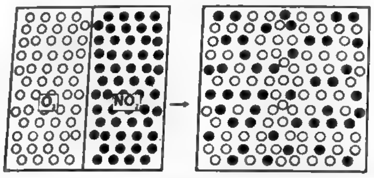
"The spontaneous mixing of the molecules of different gases by random motion and collisions to form a homogenous mixture is called diffusion."

Explanation

According to kinetic molecular theory of gases, the molecules of the gases move haphazardly. They collide among themselves, collide with the walls of the vessel and change their directions. The molecules of the gases are scattered after collisions. This spontaneous intermingling of molecules of one gas with another at a given temperature and pressure is called diffusion.

Example # 1

When two gases diffuse into each other, they wish to make their partial pressures same everywhere. Suppose NO_2, a brown coloured gas and O_2, a colourless gas, are separated from each other by a partition



DIFFUSION

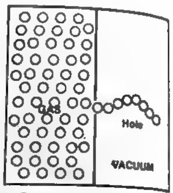
When, the partition is removed, both gases diffuse into each other due to collisions and random motion. A stage reaches when both gases generate a homogeneous mixture and partial pressures of both are uniform throughout the mixture.

Example # 2

The spreading of fragrance of rose or scent is due to diffusion.

EFFUSION

"The escape of gas molecules one by one through the hole of molecular dimension into an evacuated space without collision is called effusion."



Escape of gas molecules through a hole is EFFUSION

Explanation

The effusion of a gas is its movement through an extremely small opening into a region of low pressure. This spreading of molecules is not due to collisions but due to their tendency to escape one by one.

Actually, the molecules of a gas are habitual in colliding with the walls of the vessel. When a molecule approaches just in front of the opening, it enters the other portion of the vessel. This type of escape of molecules is called effusion.

Example

An inflated balloon gradually becomes smaller in size due to effusion.

GRAHAM'S LAW OF DIFFUSION

This law was introduced by an English scientist Thomas Graham (1805-1869).

Statement

"The rate of diffusion or effusion of a gas is inversely proportional to the square root of its density at constant temperature and pressure."

Mathematical form

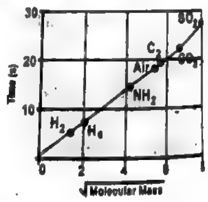
According to the law,

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}} \qquad \text{(at constant temperature and pressure)}$$

$$\text{Rate of diffusion} = \frac{k}{\sqrt{d}}$$

$$\text{Rate of diffusion} \times \sqrt{d} = k$$

or $\quad \text{Rate} \times \sqrt{d} = k$



The constant k is same for all gases, when they are all studied at the same temperature and pressure.

Let us have two gases 1 and 2, having rates of diffusion as r_1 and r_2 and densities as d_1 and d_2 respectively.

According to Graham's law,

$$r_1 \times \sqrt{d_1} = k \quad \ldots\ldots(i)$$

$$r_2 \times \sqrt{d_2} = k \quad \ldots\ldots(ii)$$

Dividing equation (i) by (ii) and rearranging,

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$

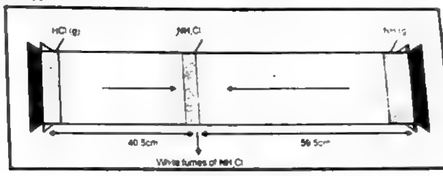
Since, the density of a given gas is directly proportional to its molecular mass. So, Graham's law can also be written as

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Where, M_1 and M_2 are molar masses of gases.

Demonstration of Graham's law

This law can be verified in the laboratory by noting the rates of diffusion of two gases in a glass tube, when they are allowed to move from opposite ends.



Verification of Graham's Law of diffusion

Two cotton plugs soaked in HCl and NH_3 solutions are introduced in the open ends of 100 cm long tube simultaneously. HCl molecules travel a distance of 40.5 cm and NH_3 molecules cover 59.5 cm in the same direction. They produce dense white fumes of NH_4Cl at point of junction. So,

$$\frac{r_{NH_3}}{r_{HCl}} = \frac{\sqrt{M_{HCl}}}{\sqrt{M_{NH_3}}}$$

$$\frac{59.5}{40.5} = \frac{\sqrt{36.5}}{\sqrt{17}}$$

$$1.46 = 1.46$$

Hence, the law is verified.

Q. Under similar conditions which of the following gases will diffuse four times as quickly as O_2

(a) He (b) N_2

(c) H_2 (d) CO_2

Contributions of some chemists in kinetic molecular theory of gases

Bernoulli (1738)

He put forward kinetic molecular theory of gases.

Clausius (1857)

- He derived the kinetic equation $PV = \frac{1}{3}mN\bar{c}^2$
- He deduced all the gas laws from kinetic equation.

Maxwell

- He elaborated and extended the kinetic molecular theory.

- He gave the law of distribution of velocities. According to this law.
  "Molecules are in the form of groups having definite velocity ranges."

Boltzmann

He contributed and studied the distribution of energies among the gas molecules.

van der Waals

He modified the general gas equation for real gases $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$

KINETIC MOLECULAR THEORY OF GASES (KMT)

"A set of postulates that describes the nature and behaviour of an ideal gas is called kinetic molecular theory of gases."

Fundamental postulates

1. Every gas consists of a large number of very small particles called molecules. Gases like He, Ne, Ar have mono-atomic molecules.
2. The molecules of a gas move haphazardly, colliding among themselves and with the walls of the container and change their directions.
3. The pressure exerted by a gas is due to the collisions of its molecules with the walls of a container. The collisions among the molecules are perfectly elastic.
4. The molecules of a gas are widely separated from one another and there are sufficient empty spaces among them.
5. The molecules of a gas have no forces of attraction for each other.
6. The actual volume of molecules of a gas is negligible as compared to the volume of gas.
7. The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them.
8. The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas.

Clausius' kinetic equation

R.J. Clausius deduced an expression for the pressure of an ideal gas. Actually, pressure on the walls of the vessel is due to collisions. Whenever, the molecules move they collide among themselves and with the walls of the container. Due to these collisions, a force is exerted on the walls of the container. This force when divided by the area of the vessel gives force per unit area, which is called pressure. In this way, the final form of kinetic equation is as follows:

$$PV=\frac{1}{3}mN\overline{c^2}$$

Where,
- P = Pressure
- V = Volume
- m = Mass of one molecule of the gas
- N = Number of molecules of gas in the vessel
- $\overline{c^2}$ = Mean square velocity

Mean square velocity

All the molecules of a gas under the given conditions don't have the same velocities. Rather different velocities are distributed among the molecules. It is explained in **Maxwell's law of distribution of velocities**. If there are n_1 molecules with velocity c_1, n_2 molecules with velocity c_2 and so on then:

$$\overline{c^2}=\frac{c_1^2+c_2^2+c_3^2+\ldots\ldots}{n_1+n_2+n_3+\ldots\ldots}$$

In this reference,

$$n_1+n_2+n_3\ \ldots\ldots=N$$

Root mean square velocity

$\overline{c^2}$ is the average of the squares of all the possible velocities. When we take the square root of this $\overline{c^2}$, then it is called root mean square velocity (C_{rms}). So,

$$C_{rms}=\sqrt{\overline{c^2}}$$

The expression for the root mean square velocity deduced from the kinetic equation is written as follows:

$$C_{rms}=\sqrt{\frac{3RT}{M}}$$

- Average velocity = $\sqrt{\frac{8RT}{\pi M}}$
- Most probable velocity = $\sqrt{\frac{2RT}{M}}$

Where,
- C_{rms} = root mean square velocity
- M = Molar mass of the gas
- T = Temperature

Conclusion

The above equation is a quantitative relationship between the absolute temperature and the velocities of the gas molecules. According to this equation, higher the temperature of a gas, greater the velocities.

Explanation of Gas Laws from Kinetic Theory of Gases

(i) Boyle's Law

According to one of the postulates of kinetic molecular theory of gases,

"The kinetic energy is directly proportional to the absolute temperature of the gas."

The kinetic energy of 'N' molecules is $\frac{1}{2}mN\overline{c^2}$

So,

$$\frac{1}{2}mN\overline{c^2}\propto T$$

$$\frac{1}{2}mN\overline{c^2}=kT \qquad \ldots\ldots(i)$$

Where 'k' is the proportional constant.

According to the kinetic equation of gases.

$$PV=\frac{1}{3}mN\overline{c^2}$$

Multiplying and dividing by 2 on right hand side

$$PV=\frac{2}{2}\left(\frac{1}{3}mN\overline{c^2}\right)$$

$$PV=\frac{2}{3}\left(\frac{1}{2}mN\overline{c^2}\right) \qquad \ldots\ldots(ii)$$

Putting eq. (i) into eq. (ii)

$$PV=\frac{2}{3}kT \qquad \ldots\ldots(iii)$$

If the temperature (T) is constant then right hand side of eq.(iii) $\frac{2}{3}kT$ is constant.

Let that constant be 'k''.

So,

$$PV=k' \qquad \text{(Boyle's law)}$$

Conclusion

At a constant temperature and number of moles, the product PV is a constant quantity.

(ii) Charles's Law

According to one of the postulates of kinetic molecular theory of gases,

"The kinetic energy is directly proportional to the absolute temperature of the gas."

The kinetic energy of 'N' molecules is $\frac{1}{2}mN\overline{c^2}$

So,
$$\frac{1}{2}mN\overline{c^2} \propto T$$
$$\frac{1}{2}mN\overline{c^2} = kT \quad \ldots\ldots (i)$$

Where 'k' is the proportional constant.

According to the kinetic equation of gases

$$PV = \frac{1}{3}mN\overline{c^2}$$

Multiplying and dividing by 2 on right hand side

$$PV = \frac{2}{2}\left(\frac{1}{3}mN\overline{c^2}\right)$$
$$PV = \frac{2}{3}\left(\frac{1}{2}mN\overline{c^2}\right) \quad \ldots\ldots (ii)$$

Putting eq. (i) into eq. (ii)

$$PV = \frac{2}{3}kT \quad \ldots\ldots (iii)$$
$$V = \left(\frac{2k}{3P}\right)T$$

At constant pressure, $\frac{2k}{3P} = k''$ *(a new constant)*

Therefore, $V = k''T$

or $\boxed{\frac{V}{T} = k''}$ (Charles's law)

Conclusion

At a constant pressure and number of moles, the ratio of V/T is a constant quantity.

(iii) Avogadro's Law

Consider two gases 1 and 2 at same pressure P and having same volume V. Their number of molecules are N_1 and N_2, *masses of molecules are* m_1 *and* m_2 *and mean square velocities are* $\overline{c_1^2}$ *and* $\overline{c_2^2}$ *respectively. Their kinetic equations can be written as follows*

For gas 1: $$PV = \frac{1}{3}m_1N_1\overline{c_1^2}$$

For gas 2: $$PV = \frac{1}{3}m_2N_2\overline{c_2^2}$$

Equating:

$$\frac{1}{3}m_1N_1\overline{c_1^2} = \frac{1}{3}m_2N_2\overline{c_2^2}$$

Hence, $$m_1N_1\overline{c_1^2} = m_2N_2\overline{c_2^2} \quad \ldots\ldots (i)$$

When the temperature of both gases is the same, their mean kinetic energies per molecule will also be same, so

$$\frac{1}{2}m_1\overline{c_1^2} = \frac{1}{2}m_2\overline{c_2^2}$$

$$m_1\overline{c_1^2} = m_2\overline{c_2^2} \quad \ldots\ldots (ii)$$

Dividing eq. (i) by eq. (ii)

$$\frac{m_1N_1\overline{c_1^2}}{m_1\overline{c_1^2}} = \frac{m_2N_2\overline{c_2^2}}{m_2\overline{c_2^2}}$$
$$N_1 = N_2$$

Conclusion

Equal volumes of all the gases at the same temperature and pressure contain equal number of molecules. This is Avogadro's law.

(iv) Graham's Law of Diffusion

According to the kinetic equation

$$PV = \frac{1}{3}mN\overline{c^2} \quad \ldots\ldots (i)$$

If we take one mole of a gas having Avogadro's number of molecules ($N = N_A$) then the equation (i) can be written

$$PV = \frac{1}{3}mN_A\overline{c^2}$$

or $$PV = \frac{1}{3}M\overline{c^2} \quad \ldots\ldots (ii) \quad (M = mN_A)$$

Where M is the molecular mass of the gas.

or $$\overline{c^2} = \frac{3PV}{M}$$

Taking square root

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3PV}{M}}$$
$$\sqrt{\overline{c^2}} = \sqrt{\frac{3P}{\frac{M}{V}}}$$
$$\sqrt{\overline{c^2}} = \sqrt{\frac{3P}{d}} \quad \left(\frac{M}{V} = d\right)$$

'V' is the molar volume of the gas at given conditions. **Since the root mean square velocity of the gas is proportional to the rate of diffusion of the gas**

$$\sqrt{\overline{c^2}} \propto r$$

So, $$r = \sqrt{\frac{3P}{d}}$$

At constant pressure,

$$r \propto \sqrt{\frac{1}{d}}$$

Which is Graham's law of diffusion.

Kinetic Interpretation of Temperature

According to kinetic molecular theory of gases the molecules of a gas move randomly. **They collide among themselves, with the walls of the vessels and change their directions. The collisions are elastic and the pressure of the gas is the result of these collisions with the walls of the container.**

Let us write the kinetic gas equation

$$PV = \frac{1}{3}mN\bar{c^2} \quad \ldots. (a)$$

Where
P = Pressure
V = Volume
m = mass of one molecule of the gas
N = Number of molecules of the gas
$\bar{c^2}$ = Mean square velocity

The average kinetic energy associated with one molecule of a gas due to its translational motion is given below

$$E_K = \frac{1}{2}m\bar{c^2} \quad \ldots (b)$$

In the above equation E_K represents the average translational kinetic energy of gas molecules.
Multiply and divide equation (a) by 2

$$PV = \frac{2}{2} \times \frac{1}{3}mN\bar{c^2}$$

$$PV = \frac{2}{3}N\left(\frac{1}{2}m\bar{c^2}\right) \quad \ldots\ldots(c)$$

Putting equation (b) into equation (c), we get

$$PV = \frac{2}{3}NE_K \quad \ldots\ldots(d)$$

If we use one mole of a gas, then $N = N_A$
Now put the value of N in the equation (d)

$$PV = \frac{2}{3}N_AE_K \quad \ldots\ldots(e)$$

According to the general gas equation for one mole of a gas

$$PV = RT$$

Put the value of PV in the equation (e)

$$RT = \frac{2}{3}N_AE_K$$

$$E_K = \frac{3R}{2N_A}T$$

But $\frac{3R}{2N_A}$ is a constant quantity. So the above equation can be written as:

$$E_K = \text{Constant} \times T$$

$$E_K \propto T$$

The above equation shows that absolute temperature or Kelvin temperature of a gas is directly proportional to the average translational kinetic energy of its molecules. This suggests that a change in temperature means change in the intensity of molecular motion.

Idea of flow of heat:

When heat flows from one body to another body, the molecules in the hotter body give up some of their kinetic energy through collisions to the molecules in the colder body. This process of flow of heat continues until the average translational kinetic energies of all the molecules in both bodies become equal.

- ***In gases and liquids**, temperature is the measure of average translational kinetic energies of molecules.*
- ***In solids**, where molecules cannot move freely temperature becomes a measure of vibrational kinetic energy*

Absolute zero

If we look at the absolute zero in the light of kinetic interpretation, we can say that it is that temperature at which the molecular motions cease. The absolute zero is unattainable. However current attempts have resulted in a temperature as low as 10^{-5} K.

LIQUEFACTION OF GASES

General Principle of Liquefaction

The conversion of a gas into a liquid requires high pressure and low temperature. High pressure brings molecules of a gas close to each other. Low temperature deprives the molecules from kinetic energy and attractive forces start dominating

Critical Temperature (T_c)

"The highest temperature at which a substance can exist as a liquid is called critical temperature."

or

"The temperature of a gaseous substance above which it cannot be converted into the liquid state no matter how much the pressure is applied on it is called critical temperature

Factors affecting the critical temperature

The value of the critical temperature of a substance depends upon.

(i) Size of the molecule
(ii) Shape of the molecule
(iii) Intermolecular forces

Critical Pressure (P_c)

"The pressure which is required to bring about liquefaction at critical temperature is called critical pressure."

Critical Temperatures and Critical Pressures of Some Substances

Substance	Critical Temperature T_c(K)	Critical Pressure P_c (atm)
Water vapours, H_2O	647.6 (374.44°C)	[illegible]
Ammonia, NH_3	405.6 (132.44°C)	[illegible]
Freon-12, CCl_2F_2	384.7 (111.54°C)	[illegible]
Carbon dioxide, CO_2	304.3 (31.142°C)	[illegible]
Oxygen, O_2	154.4 (−118.75°C)	[illegible]
Argon, Ar	150.9 (−122.26°C)	[illegible]
Nitrogen, N_2	126.1 (−147.06°C)	[illegible]
Hydrogen, H_2	33.2 (-239.96°C)	[illegible]
Helium, He	5.3 (-267.86°C)	2.26

Importance of critical temperature and critical pressure

The critical temperature and the critical pressure of the substances are very important for the workers dealing with the gases. These properties provide us the information about the conditions under which gases liquefy

For examples

(i) O_2 has a critical temperature 154.4 K (−118.75°C). **It must be cooled below this temperature before it can be liquefied by applying high pressure.**

(ii) Ammonia is a polar gas. Its critical temperature is 405.6K (132.44°C), so it can be liquefied by applying sufficient pressure close to room temperature.

Critical Volume (V_c)

"When a gas is measured at its critical temperature and critical pressure, then at that stage volume of 1 mole of gas is called critical volume."

Substance	Critical Volume ($cm^3\ mol^{-1}$)
Oxygen (O_2)	74.42 $cm^3\ mol^{-1}$

Carbon dioxide (CO_2)	95.65 $cm^3\ mol^{-1}$
Hydrogen (H_2)	64.51 $cm^3\ mol^{-1}$

Q15. Explain the following facts:

(iv) Water vapors do not behave ideally at 273K.

Ans. Any gas kept below its critical temperature behave non-ideally because under these conditions, forces of attraction can dominate and gas is converted into liquid by applying pressure. Since, water vapours are kept at 273K below their critical temperature (374.44 °C), hence are converted into liquid by applying the pressure because vapours have sufficient intermolecular forces between them under these conditions.

Methods of Liquefaction of Gases

Following methods are generally used to liquefy gases.

(i) Faraday's method (The gases liquefied by this method had their critical temperature above or just below the ordinary atmospheric temperature).

(ii) Claude's method (The gas is cooled not only by overcoming the intermolecular forces but also by performance of work).

(iii) Linde's method (Linde has employed Joule-Thomson effect as the basis for liquefaction).

Joule Thomson Effect

"When a compressed gas is allowed to expand into a region of low pressure, it gets cooled."

- Low temperature can be achieved by Joule Thomson effect.

Explanation

The molecules of a compressed gas are very close to each other and appreciable attractive forces are present among them. When a gas is allowed to undergo sudden expansion through the nozzle of a jet, then the molecules move apart. In this way, energy is needed to overcome the intermolecular attractions. This energy is taken from the gas itself, which is cooled.

Q. What is the basis of Joule-Thomson effect?

Linde's method of Liquefaction of Gases

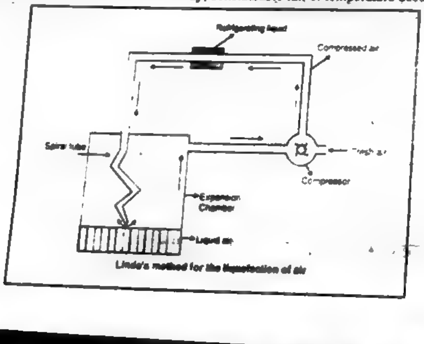
Linde has employed Joule-Thomson effect as the basis for liquefaction.

Compression

For the liquefaction of air, it is compressed to about 200 atm and then passed through a water cooled pipe where the heat of compression is removed.

Expansion

It is then allowed to pass through a spiral pipe having a jet at the end. When air comes out of the jet, the expansion takes place from 200 atm to 1 atm. In this way, considerable fall of temperature occurs.



Linde's method for the liquefaction of air

Collection

This cooled air goes up and cools the incoming compressed air. It returns to the compression pump. This process is repeated again and again. The liquid air is collected at the bottom of the expansion chamber.

Limitation of Linde's method

By this method, we cannot liquefy H_2 and He gases.

Differentiate between ideal and non-ideal gases

Ans.

Ideal Gases	Non-ideal Gases
Those gases which obey gas laws under all conditions of temperature and pressure are called ideal gases	Those gases which do not obey gas laws under all conditions of temperature and pressure are called non-ideal gases.
There is no force of attraction among their molecules	Force of attraction is present among the molecules of non-ideal gases
Ideal gases can never be liquefied.	These gases can be liquefied
The volume of ideal gases may be equal to zero	The volume of non-ideal gases can never be equal to zero
Ideal gases do not exist in nature.	All real gases like H_2, O_2, N_2 etc. are non-ideal

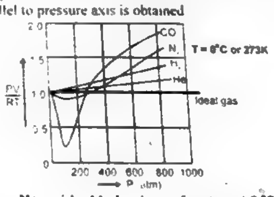
NON-IDEAL BEHAVIOUR OF GASES

The behaviour of the real gases like H_2, He, N_2 and CO_2 is studied keeping in view the [illegible] pressure on the gas and the change in its volume.

Compressibility factor

First of all, a graph is plotted between pressure on X-axis and the PV / nRT on Y-axis [illegible]. The factor PV / nRT is called the compressibility factor. Its **value is unity under all conditions for an ideal gas**.

- For an **ideal gas** the increase of pressure decreases the volume such that PV / nRT remains constant at a constant temperature, so a straight line parallel to pressure axis is obtained.



Non - ideal behaviour of gases at 0 °C.

- All the real gases have been found to show marked deviation from this behaviour.

Graphical Explanation (at 0°C)

- **For He gas**, graph goes along with expected horizontal line to some extent but goes above this line at very high pressures. It means that at very high pressure, the decrease in volume is not according to general gas equation and the value of PV / nRT has increased from the expected values. With this type of behaviour, we would say that the gas is non-ideal.
- **For H_2 gas**, the deviation starts even at low pressure in comparison to He.
- **N_2 gas** shows a decrease in PV / nRT value at the beginning and shows marked deviation even at low pressure than H_2.
- **CO_2 gas** has a very strange behaviour as it is evident from the graph.

Limitations for gases

The extent of deviation of these four gases shows that these gases have their own limitations for obeying general gas equation. It depends upon the nature of the gas that at which value of pressure, it will start disobeying.

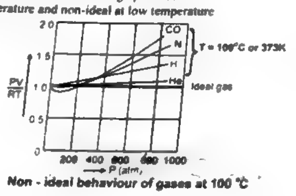
Graph at 100 °C

If the behaviour of all these four gases at elevated temperature i.e. 100°C is studied, then the graphs come closer to the expected straight line and the deviations are shifted towards higher pressure. This means that the increase in temperature makes the gases ideal.

Conclusion

This discussion on the basis of experimental observations convinces us that:

- Gases are ideal at low pressure and non-ideal at high pressure
- Gases are ideal at high temperature and non-ideal at low temperature



Non - ideal behaviour of gases at 100 °C

Causes for deviations from ideality

van der Waals (1873) attributed the deviation of real gases from ideal behaviour to two of the eight postulates of kinetic molecular theory of gas.

Faulty postulates of KMT of gases:

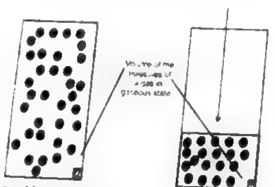
These postulates are as follows.

(i) There are no forces of attraction among the molecules of a gas.

(ii) The actual volume of gas molecules is negligible as compared to volume of vessel.

Explanation

- When the pressure on a gas is high and the temperature is low then the attractive forces among the molecules becomes significant, so the ideal gas equation $PV = nRT$ does not hold. Actually, under these conditions, the gas does not remain ideal.
- The actual volume of the molecules of a gas is usually very small as compared to the volume of the vessel and hence it can be neglected. This volume, however, does not remain negligible when the gas is subjected to high pressure as shown in the figure below.



A gas at low pressure when actual volume is negligible

A gas at high pressure when actual volume is not negligible.

Q13b. Do you think that some of the postulates of kinetic molecular theory of gases are faulty? Point out these postulates.

Ans. Kinetic molecular theory quantitatively explains the behaviour of gases.

If a gas follows general gas equation $PV = nRT$ under all conditions of temperature and pressure it is ideal and obeys all postulates of kinetic molecular theory of gases. On the other hand, high pressure brings the gas molecules close to each other and low temperature deprives them from their kinetic energy. It develops attractive forces among their molecules causing a non-ideal behaviour.

Under a highly compressed condition, the actual volume is not negligible as compared to the volume of vessel.

According to above discussion, two postulates of KMT of gases are considered faulty. They are

(i) There are no forces of attraction among the molecules of a gas

(ii) Actual volume of gas molecule is negligible as compared to the volume of the vesse.

Q. The value of compressibility factor for H_2 and He is always positive. Justify.

Ans. The behaviour of H_2 and He is exceptional because the compressibility factor always increases with increase in pressure. This is due to the fact that 'a' for hydrogen and helium are very small indicating that forces of attraction in these gases are very weak. Therefore, (an^2 / V^2) is negligible at all pressures so that Z is always greater than one.

van der Waals's Equation for Real Gases

van der Waals pointed out that both pressure and volume factors in ideal gas equation needed correction to make it applicable to the real gases.

Volume Correction

(i) Compression of a gas

When a gas is compressed, the molecules are pushed so close together that the repulsive forces operate between them. When pressure is increased further, it is opposed by the molecules themselves. Actually, the molecules have definite volume, no doubt, very small as compared to the vessel, but it is not negligible.

(ii) van der Waals's postulate

van der Waals postulated that the actual volume of molecules can no longer be neglected in a highly compressed gas. If the **effective volume** of the molecules per mole of a gas is represented by b, then the volume available to gas molecules is the volume of the vessel minus the volume of gas molecules

$$V_{free} = V_{vessel} - b$$

Where, "V_{free}" is the volume available to gas molecules.

(iii) Excluded Volume "b"

"The volume of a gas which is occupied by 1 mole of gas molecules in highly compressed state, but not in the liquid state, is called excluded volume or effective volume or incompressible volume (b)."

- It is a constant and characteristic of a gas.
- Its value depends upon the size of the gas molecules.
- It is also a van der Waals constant.
- It is not equal to the actual volume of gas molecules. In fact, it is four times the actual volume of molecules.

$$b = 4\,V_m$$

Where, V_m is actual volume of one mole of gas molecules

Value of "b" for some common gases

Gas	'b' ($dm^3\,mol^{-1}$)
Hydrogen	0.0266
Oxygen	0.0318
Nitrogen	0.0391
Carbon dioxide	0.0428
Ammonia	0.0371
Sulphur dioxide	0.0564
Chlorine	0.0562

Pressure correction

(i) Attraction between molecules

A molecule in the interior of a gas is attracted by other molecules on all sides, so these attractive forces are cancelled out. However, when a molecule strikes the wall of a container, it experiences a force of attraction towards the other molecules in the gas. This decreases the force of its impact on the wall.

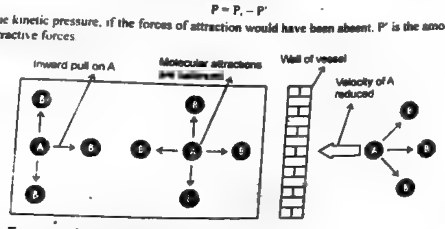
(ii) Pressure on the wall of container

Consider a molecule "A" which is unable to create pressure on the wall due to the presence of attractive forces due to "B" type molecules. Let the observed pressure on the wall of the container is "P"

This pressure is less than the actual pressure P_i by an amount P'. So,

$$P = P_i - P'$$

Where P_i is the true kinetic pressure, if the forces of attraction would have been absent. P' is the amount of pressure lessened due to attractive forces.



Forces of attraction and pressure correction.

Ideal pressure P_i is

$$P_i = P + P'$$

It is suggested that a part of the pressure "P" for one mole of a gas used up against intermolecular attractions should decrease as volume increases.

(iii) Value of P'

The value of P' in terms of a constant "a" which accounts for the attractive forces and the volume V of vessel can be written as

$$P' = \frac{a}{V^2}$$

How to prove it

P' is determined by the forces of attraction between molecules of type A, which are striking the wall of the container and molecules of type B, which are pulling them inward. The net force of attraction is proportional to the concentrations of A type and B type molecules.

$$P' \propto C_A \cdot C_B$$

Let, n is the number of moles of A and B separately and total volume of both types of molecules is "V". Then n/V is moles dm^{-3} of A and B, separately

$$P' \propto \frac{n}{V} \cdot \frac{n}{V}$$

$$P' \propto \frac{n^2}{V^2}$$

$$P' = \frac{an^2}{V^2}$$

For n = 1,

$$P' = \frac{a}{V^2} \quad \text{......(i)}$$

Greater the attractive forces among the gas molecules, smaller the volume of vessel, greater the value of lessened pressure P'. "a" is coefficient of attraction or attraction per unit volume. It has a constant value for a particular real gas. The effective kinetic pressure of a gas is given by P_i, which is the pressure if the gas would have been ideal.

$$P_i = P + P' \quad \text{... (ii)}$$

Putting values of P' from equation (i) into (ii)

$$P_i = P + \frac{a}{V^2}$$

Value of "a" for some common gases

Gas	'a' ($atm\,dm^6\,mol^{-2}$)
Hydrogen	0.245
Oxygen	1.360
Nitrogen	1.390
Carbon dioxide	3.590
Ammonia	4.170
Sulphur dioxide	6.170
Chlorine	6.493

For one mole of a gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For "n" moles of a gas

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

This is called van der Waals's equation. 'a' and 'b' are called van der Waals's constants.

(a) Common units of 'a':

Since $P' = \frac{an^2}{V^2}$

So $a = \frac{P'V^2}{n^2}$

If $P' = atm$, $V = dm^3$, $n = mol$

then $a = \frac{atm.(dm^3)^2}{(mol)^2}$

Common units of a = **atm dm^6 mol^{-2}**

(b) SI units of 'a'

Since in SI,

$P' = Nm^{-2}$, $V = m^3$, $n = mol$

So $a = \frac{P'V^2}{n^2}$

$$= \frac{Nm^{-2} \times (m^3)^2}{(mol)^2} = \frac{Nm^{-2}.m^6}{mol^2}$$

SI units of a = **Nm^{4} mol^{-2}**

(c) Common units of 'b'

b = Excluded volume mol^{-1} of a gas

So **$b = dm^3\,mol^{-1}$** [As $V = dm^3$]

(d) SI units of 'b'

$b = m^3\,mol^{-1}$ [As $V = m^3$]

Determination and dependence of value of "a" and "b"

The values of 'a' and 'b' can be determined by knowing the values of P, V and T of a gaseous system under two different conditions.

$b = 4V_m$

$P' = \frac{an^2}{V^2}$

$P'V^2 = an^2$

- The presence of intermolecular forces in gases like Cl_2 and SO_2 increases their 'a' factor. The least value of 'a' for H_2 is due to its small size and non-polar character
- The 'b' value of H_2 is 0.0266 $dm^3 mol^{-1}$. It means that if 2.016g (1mole) of H_2 is taken, then it will occupy 0.0266 dm^3 or $26.6cm^3$ of volume at closest approach in the gaseous state

Q13c. Hydrogen and Helium are ideal at room temperature but SO_2 and Cl_2 are non-ideal. How will you explain this.

Ans. If a gas is non polar, having weak intermolecular forces, it means that the gas is behaving ideally (The values of 'a' and 'b' are small for that gas)

The presence of intermolecular forces in gases like Cl_2 and SO_2 increases their 'a' factor, making them non-ideal as compared to H_2 and He (small size and non-polar). Similarly excluded volumes of Cl_2 and SO_2 are greater due to large size of molecules, again making them non-ideal. H_2 and He have less values of 'b' so they behave ideally at room temperature

Q14b. What is the physical significance of van der Waals's constants 'a' & 'b'. Give their units.

Ans. Physical Significance of 'a' and 'b':

- In van der Waals's equation, 'a' is called co-efficient of attraction or attraction per unit volume. It has a constant value for a particular real gas. Higher the value of 'a', stronger the intermolecular forces and more deviation from ideal behaviour
- In van der Waals's equation 'b' is excluded or incompressible or effective volume per mole of a gas. Its value depends upon the size of gas molecule. Higher the value of 'b', greater the size of gas molecules and more deviation from ideal behaviour

Note Units are given above in topic

Q15. Explain the following facts:

(iii) Pressure of NH_3 gas at given conditions (say 20 atm pressure and room temperature) is less as calculated by van der Waals's equation than that calculated by general gas equation.

Ans. Ammonia being a polar gas has a greater value of 'a' (attractive co-efficient = 4.17 atm dm^6 mol^{-2}). Due to intermolecular forces, it behaves as a non-ideal gas. Therefore the pressure calculated by van der Waal's equation is less than that calculated by general gas equation

(v) SO_2 is comparatively non-ideal at 273K but behaves ideally at 327°C.

Ans. Any real gas can behave ideally or non-ideally depending upon conditions of temperature and pressure. As we know gases are ideal at high temperature and non-ideal at low temperature. SO_2 has a large size and a polar gas. So it has strong intermolecular forces. Therefore at 273K (0°C), it shows non-ideal behaviour due to strong intermolecular forces. It behaves ideally at 327°C (600 K) due to weak intermolecular forces.

PLASMA STATE

What is plasma?

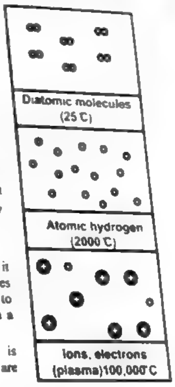
Plasma is often called the "fourth state of matter", the other three being solid, liquid and gas. Plasma was identified by the English scientist William Crookes in 1879. In addition to being important in many aspects of our daily life, plasmas are estimated to constitute more than 99 percent of the visible universe. Although, naturally occurring plasma is rare on earth, there are many man – made examples. Inventors have used plasma to conduct electricity in neon signs and fluorescent bulbs. Scientists have constructed special chambers to experiment with plasma in laboratories. It occurs only in lightning discharges and in artificial devices like fluorescent lights, neon signs, etc. It is everywhere in our space environment

How is Plasma formed?

When more heat is supplied, the atoms or molecules may be ionized. An electron may gain enough energy to escape its atom. This atom loses one electron and develops a net positive charge. It becomes an ion. In a sufficiently

heated gas, ionization happens many times, creating clouds of free electrons and ions. However all the atoms are not necessarily ionized, and some of them may remain completely intact with no net charge. This ionized gas mixture consisting of ions, electrons and neutral atoms is called plasma.

It means that a plasma is a distinct state of matter containing a significant number of electrically charged particles a number sufficient to affect its electrical properties and behaviour.



Natural and Artificial Plasma

Artificial plasma can be created by ionization of a gas, as in neon signs. Plasma at low temperatures is hard to maintain because outside a vacuum low temperature plasma reacts rapidly with any molecule it encounters. This aspect makes this material, very useful and hard to use.

Natural plasma exists only at very high temperatures, or low temperature vacuums

Natural plasma on the other hand do not breakdown or react rapidly, but is extremely hot (over 20,000°C minimum). Their energy is so high that they vaporize any material they touch

Characteristic of Plasma

1. A plasma must have sufficient number of charged particles so as a whole, it exhibits a collective response to electric and magnetic fields. The motion of the particles in the plasma generate fields and electric currents from within plasma density. It refers to the density of the charged particles. This complex set of interactions makes plasma a unique, fascinating, and complex state of matter.
2. Although plasma includes electrons and ions and conducts electricity, it is macroscopically neutral. In measurable quantities the number of electrons and ions are equal.

Where is Plasma found?

Entire universe is almost of plasma. It existed before any other forms of matter came into being. Plasmas are found in everything from the sun to quarks, the smallest particles in the universe.

As stated earlier plasma is the most abundant form of matter in the universe. It is the stuff of stars. A majority of the matter in inner-steallar space is plasma. All the stars that shine are all plasma. The sun is a 1.5 million kilometer ball of plasma, heated by nuclear fusion.

On earth it only occurs in a few limited places, like lightning bolts, flames, auroras, and fluorescent lights. When an electric current is passed through neon gas, it produces both plasma and light

Applications of Plasma

Plasma has numerous important technological applications. It is present in many devices. It helps us to understand much of the universe around us. Because plasmas are conductive respond to electric and magnetic fields and can be efficient sources of radiation, so they can be used in innumerable applications where such control is needed or when special sources of energy or radiation are required.

(i) A fluorescent light bulb is not like regular light bulbs. Inside the long tube is a gas. When the light is turned on, electricity flows through the tube. This electricity acts as that special energy and charges up the gas. This charging and exciting of the atoms creates a glowing plasma inside the bulb.

(ii) Neon signs are glass tubes filled with gas. When they are turned on then the electricity flows through the tube. The electricity charges the gas, possibly neon, and creates a plasma inside the tube. The plasma glows with a special colour depending on what kind of gas is inside.

(iii) They find applications such as plasma processing of semiconductors, sterilization of some medical products, lamps, lasers, diamond coated films, high power microwave sources and pulsed power switches

(iv) They also provide the foundation for important potential applications such as the generation of electrical energy from fusion pollution control and removal of hazardous chemicals

(v) Plasma light up our offices and homes, make our computers and electronic equipment work.

(vi) They drive lasers and particle accelerators, help to clean up the environment, pasteurize foods and make tools corrosion-resistant

Future Horizons

Scientists are working on putting plasma to effective use. Plasma would have to be low energy and should be able to survive without instantly reacting and degenerating. The application of magnetic fields involves the use of plasma. The magnetic fields create low energy plasma which creates molecules that are in what scientist call a metastable state. The magnetic fields used to create the low temperature plasma give the plasma molecules, which do not react until they collide with another molecule with just the right energy. This enables these metastable molecules to survive long enough to react with a designated molecule.

These metastable particles are selective in their reactivity. It makes them a potentially unique solution to problems like radioactive contamination.

Scientist are currently experimenting with mixtures of gases to work as metastable agents on plutonium and uranium, and this is just the beginning.

KEY POINTS

1) The behaviour of a gas is described through four variables i.e., pressure, volume, temperature and its number of moles. The relationships between gas variables are known as the simple gas laws. Boyle's law related pressure of a gas with its volume, while Charles's law relates gas volume with temperature. Avogadro's law is concerned with volume and amount of a gas. The important concept of absolute zero of temperature originates from the simple gas laws.

2) By combining the above mentioned three laws, a more general equation about the behaviour of gas is obtained i.e., $PV = nRT$. This equation can be solved for any one of the variables when values for others are known. This equation can be modified for the determination of molar masses and the density of the gas.

3) Dalton's law of partial pressures can be used to calculate the partial pressures of gases.

4) The processes of diffusion and effusion are best understood by Graham's law of diffusion.

5) Kinetic molecular theory of gases provides a theoretical basis for various gas laws. With the help of this theory a relationship is established between average molecular kinetic energy and kelvin temperature. The diffusion and effusion of the gases can be related to their molar masses through the kinetic molecular theory of gases.

6) The real gases show ideal behaviour under specific conditions. They become non-ideal at high pressure and low temperature. The non-ideal behaviour results chiefly from intermolecular attractions and the finite volume occupied by the gas molecules.

7) Gases can be liquefied by applying sufficient pressure but temperature should either by critical one or below it.

8) To calculate the pressure or volume of a real gas under the non-ideal conditions, alternative kinetic equation has been developed. This is known as the van der Waals's equation.

9) The plasma, a forth state of matter, consist of neutral particles, positive ions and negative electrons, 99% of the known universe is in the plasma state.

SOLVED OBJECTIVE EXERCISE

Q1: Select the correct answer out of the following alternative suggestions.

(i) Pressure remaining constant, at which temperature the volume of a gas will become twice of what it is at 0°C.

(a) 546°C (b) 200°C
(c) 546 K (d) 273 K

(ii) Number of molecules in one dm^3 of water is close to

(a) $\frac{6.02}{22.4}\times10^{23}$ (b) $\frac{12.04}{22.4}\times10^{23}$
(c) $\frac{18}{22.4}\times10^{23}$ (d) $55.6\times6.02\times10^{23}$

(iii) Which of the following will have the same number of molecules at STP?

(a) 280 cm^3 of CO_2 and 280 cm^3 of N_2O
(b) 11.2 dm^3 of O_2 and 32 g of O_2
(c) 44 g of CO_2 and 11.2 dm^3 of CO
(d) 28 g of N_2 and 5.6 dm^3 of oxygen

(iv) If absolute temperature of a gas is doubled and the pressure is reduced to one half, the volume of the gas will

(a) Remain unchanged (b) Increase four times
(c) Reduce to 1/4 (d) be doubled

(v) How should the conditions be changed to prevent the volume of a given gas from expanding when its mass is increased?

(a) Temperature is lowered and pressure is increased.
(b) Temperature is increased and pressure is lowered.
(c) Temperature and pressure both are lowered.
(d) Temperature and pressure both are increased.

(vi) The molar volume of CO_2 is maximum at

(a) STP (b) 127°C and 1 atm
(c) 0°C and 2 atm (d) 273°C and 2 atm

(vii) The order of the rate of diffusion of gases NH_3, SO_2, Cl_2 and CO_2 is

(a) $NH_3 > SO_2 > Cl_2 > CO_2$ (b) $NH_3 > CO_2 > SO_2 > Cl_2$
(c) $Cl_2 > SO_2 > CO_2 > NH_3$ (d) $NH_3 > CO_2 > Cl_2 > SO_2$

(viii) Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of total pressure exerted by oxygen is

(a) 1/3 (b) 8/9
(c) 1/6 (d) 1/9

(ix) Gases deviate from ideal behaviour at high pressure. Which of the following is correct for non-ideality?

(a) At high pressure, the gas molecules move in one direction only.
(b) At high pressure, the collisions between the gas molecules are increased manifold
(c) At high pressure, the volume of the gas becomes insignificant.
(d) At high pressure, the intermolecular attractions become significant.

(x) The deviation of a gas from ideal behaviour is maximum at

(a) −10°C and 5.0 atm (b) −10°C and 2.0 atm
(c) 100°C and 2.0 atm (d) 0°C and 2.0 atm

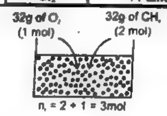
(xi) A real gas obeying van der Waals equation will resemble the ideal gas if

(a) Both 'a' and 'b' are large (b) Both 'a' and 'b' are small
(c) 'a' is small and 'b' is large (d) 'a' is large and 'b' is small

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	**(c) 546 K**	If at 0°C (273K) the volume is x then at 273°C (546K) the volume will become 2x.
(ii)	**(d) $55.6 \times 6.02 \times 10^{23}$**	$1 dm^3$ water = 1000g = 1000/18 = 55.5mol 1 mol of water = 6.022×10^{23} molecules 55.5 mol of water = $55.5 \times 6.022 \times 10^{23}$
(iii)	**(a) 280 cm^3 of CO_2 and 280 cm^3 of N_2O**	According to Avogadro's law "Equal volumes of all the ideal gases at the same temperature and pressure contain equal number of molecules." At STP 280 cm^3 of CO_2 and 280 cm^3 of N_2O have equal volume so they have same number of molecules.
(iv)	**(b) Increase four times**	PV = nRT $V = \frac{nRT}{P} = \frac{T}{P} = \frac{2}{\frac{1}{2}}$ $\boxed{V = 4}$
(v)	**(a) Temperature is lowered and pressure is increased.**	An increase in pressure decreases the volume. Similarly a decrease in temperature also decreases the volume.
(vi)	**(b) 127°C and 1 atm**	$PV = nRT \Rightarrow V = \frac{nRT}{P} \Rightarrow V = \frac{T}{P}$ (a) $V = \frac{273}{1} = 273$ (b) $V = \frac{400}{1} = 400$ (c) $V = \frac{273}{2} = 136.5$ (d) $V = \frac{546}{2} = 273$
(vii)	**(b) $NH_3 > CO_2 > SO_2 > Cl_2$**	According to Graham's law of diffusion $\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$ Greater the molecular mass lesser will be rate of diffusion and vice versa.

Gas	Molecular Mass
NH_3	17 amu
CO_2	44 amu
SO_2	64 amu
Cl_2	71 amu

Q. No	Answer	Reason
(viii)	**(a) 1/3**	 $p_{O_2} = \frac{1}{3}$ $p_{CH_4} = \frac{2}{3}$
(ix)	**(d) At high pressure, the intermolecular attractions become significant.**	Significant attractive forces are present between molecules in non ideal gases. So when we increase the pressure it brings gas molecules close to each other and hence attractive forces operate between molecules.

(x)	**(a) –10°C and 5.0 atm**	High pressure and low temperature are conditions for deviation of gases from ideal behavior.
(xi)	**(b) Both 'a' and 'b' are small**	According to van der Waals's equation $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$ For an ideal gas a = 0, b = 0 So $\left(P + \frac{n^2(0)}{V^2}\right)(V - n(0)) = nRT$ PV = nRT it is applicable for ideal gases at all conditions of temperature and pressure

Q2. Fill in the blanks:

(i) The product PV has the S.I. unit of ________.

(ii) Eight grams of each O_2 and H_2 at 27°C will have total K.E in the ratio of ________

(iii) Smell of the cooking gas during leakage from a gas cylinder is due to the property of ________ of gases

(iv) Equal ________ of ideal gases at the same temperature and pressure contain ________ number of molecules

(v) The temperature above which a substance exists only as a gas is called ________

ANSWERS

(i) Nm	(ii) 1 : 16
(iii) diffusion	(iv) volume, equal
(v) critical temperature (T_c)	

Q3. Tick true and false:

(i) Kinetic energy of molecules of gas is zero at 0°C.

(ii) A gas in a closed container will exert much higher pressure at the bottom due to gravity than at the top

(iii) Real gases show ideal gas behaviour at low pressure and high temperature

(iv) Liquefaction of gases involves decrease in intermolecular spaces

(v) An ideal gas on expansion will show Joule-Thomson effect.

ANSWERS

(i) False	(ii) False	(iii) True	(iv) True	(v) False

NUMERICAL OF EXERCISE

Q5. (b) A sample of carbon monoxide gas occupies 150 mL at 25°C. It is then cooled at constant pressure until it occupies 100 mL. What is the new temperature?

Ans. **Given data:**

Initial volume $= V_1 = 150\ cm^3$

Initial temperature $= T_1 = 25°C + 273 = 298K$

Final volume $= V_2 = 100\ cm^3$

Required:

Final temperature $= T_2 = ?$

Solution:

According to Charles's law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_2 = \frac{V_2T_1}{V_1} = \frac{100 \times 298}{150}$$

$$= 198.67\ K$$

Final temperature = T_2 = 198.67 K or 198.67 − 273 = −74.33°C

Q16. Helium in a 100 cm³ container at a pressure of 500 torr is transferred to a container with a volume of 250 cm³. What will be the new pressure?

(a) If no change in temperature occurs.

(b) If temperature changes from 20°C to 15°C.

Ans. ***Given data:***

Initial volume $= V_1 = 100\ cm^3$

Initial pressure $= P_1 = 500$ torr

Final volume $= V_2 = 250\ cm^3$

(a) Required:

Final pressure $= P_2 = ?$

Solution:

According to Boyle's law

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{500 \times 100}{250}$$

$$= 200\ torr$$

(b) Given data:

Initial volume $= V_1 = 100\ cm^3$

Initial pressure $= P_1 = 500$ torr

Final Volume $= V_2 = 250\ cm^3$

Initial temperature $= T_1 = 20°C + 273 = 293\ K$

Final temperature $= T_2 = 15°C + 273 = 288\ K$

Required:

Final pressure $= P_2 = ?$

Solution:

According to General gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_2 = \frac{P_1V_1T_2}{V_2T_1} = \frac{500 \times 100 \times 288}{250 \times 293}$$

$$= 196.58\ torr$$

(a) Final pressure = 200 torr

(b) Final pressure = 196.58 torr

Q17. (a) What are densities in kg m⁻³ of the following at STP?
(P = 101325Nm⁻², T=273K, molecular masses are in kg mol⁻¹)
(i) methane, (ii) oxygen, (iii) hydrogen

Ans. **Given data:**

Pressure $= 101325\ Nm^{-2}$

Temperature $= 0°C + 273\ K$

R = General gas constant $= 8.3143\ Nm\ mol^{-1}\ K^{-1}$

Molar masses of gases:

(i) CH_4 $= 16\ g\ mol^{-1} = 0.016\ kg\ mol^{-1}$

(ii) O_2 $= 32\ g\ mol^{-1} = 0.032\ kg\ mol^{-1}$

(iii) H_2 $= 2\ g\ mol^{-1} = 0.002\ kg\ mol^{-1}$

Required:

Density of CH_4 = ?

Density of O_2 = ?

Density of H_2 = ?

Solution:

$$d = \frac{PM}{RT}$$

(i) Density of CH_4 $= \frac{101325 \times 0.016}{8.3143 \times 273}$

$= 0.714\ kg\ m^{-3}$

(ii) Density of O_2 $= \frac{101325 \times 0.032}{8.3143 \times 273}$

$= 1.428\ kg\ m^{-3}$

(iii) Density of H_2 $= \frac{101325 \times 0.002}{8.3143 \times 273}$

$= 0.0892\ kg\ m^{-3}$

Density of CH_4 = 0.714 kg m⁻³

Density of O_2 = 1.428 kg m⁻³

Density of H_2 = 0.0892 kg m⁻³

(b) Compare the values of densities in proportion to their molar masses.

Ans. Molar masses of these gases are in an order

$H_2 < CH_4 < O_2$

According to equation

$$d = \frac{PM}{RT}$$

If P, R and T are constant then $d \propto M$.

We will observe that densities are also in the same order because greater the molar mass of gas, greater will be its density and vice versa

(c) How do you justify that increase in volume upto 100 dm³ at 27°C of 2 moles of NH_3 will allow the gas behave ideally as compared to STP conditions.

Ans. A real gas behaves more ideally under two conditions:

(i) Low pressure

(ii) High temperature.

According to statement the NH_3 gas at STP should occupy $22.414\ dm^3 \times 2 = 44.818\ dm^3$. As temperature is increased from 0°C to 27°C and volume is increased from 44.818 dm³ to 100 dm³, conditions are suitable for NH_3 to show ideal behaviour at 27°C occupying 100 dm³ than at 0°C occupying 44.818 dm³.

Q18. A sample of krypton with a volume of 6.25 dm^3 and a pressure of 765 torr and a temperature of 20°C is expanded to a volume of 9.55 dm^3 and a pressure of 375 torr. What will be the new temperature in °C?

Ans. Given data:

Initial volume $= V_1 = 6.25\ dm^3$
Final volume $= V_2 = 9.55\ dm^3$
Initial pressure $= P_1 = 765$ torr
Final pressure $= P_2 = 375$ torr
Initial temperature $= T_1 = 20°C + 273 = 293\ K$

Required:

Final temperature $= T_2 = ?$

Solution:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$T_2 = \frac{P_2V_2T_1}{P_1V_1} = \frac{375 \times 9.55 \times 293}{765 \times 6.25}$$

$= 219.46\ K$

$219.46\ K - 273 = -53.5°C$

Final temperature $= T_2 = -53.5°C$

Q19. Working at a vacuum line a chemist isolated a gas in weighing bulb with a volume of 255 cm^3 at a temperature of 25°C and under a pressure of 10.0 torr. The gas weighed 12.1 mg. What is the formula mass of this gas?

Ans. Given data:

Volume of gas = V $= 255\ cm^3$

$= \frac{255}{1000} = 0.255\ dm^3$

Pressure of gas = P $= 10.0$ torr

$= \frac{10}{760} = 0.0132$ atm

Temperature = T $= 25°C + 273 = 298\ K$

Mass of gas = m $= 12.1$ mg

$= 12.1 \times 10^{-3}\ g\ [1\ mg = 10^{-3}\ g]$

R $= 0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1}$

Required:

Molar mass M = ?

Solution:

According to general gas equation

$$PV = \frac{m}{M}RT$$

$$M = \frac{mRT}{PV} = \frac{12.1\times10^{-3}\times0.0821\times298}{0.0132\times0.255}$$

$= 87.94\ g\ mol^{-1}$

Molar mass of gas = $87.94\ g\ mol^{-1}$

Q20. What pressure is exerted by a mixture of 2.00 g of H_2 and 8.00 g of N_2 at 273 K in a 10 dm^3 vessel?

Ans. Given data:

Mass of H_2 $= 2.00$ g
Mass of N_2 $= 8.00$ g
Volume of gas $V = 10\ dm^3$

Temperature $= T = 273\ K$
R (general gas constant) $= 0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1}$

Required:

Pressure = P = ?

Solution:

According to General gas equation

$PV = nRT$

We should first calculate the number of moles of H_2 and N_2 then add them to get total number of moles

Number of moles $= \frac{\text{mass in g}}{\text{mol mass}}$

Number of moles of H_2 $= \frac{2.0}{2} = 1$ mole

Number of moles of N_2 $= \frac{8.0}{28} = 0.286$ moles

n = Total moles $= 1 + 0.286 = 1.286$

Now we can calculate pressure

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{1.286\times0.0821\times273}{10}$$

$$P = \frac{28.82}{10} = 2.88\ atm$$

Pressure of mixture of gases is = 2.88 atm

Q21. (a) The relative densities of two gases A and B are 1 : 1.5. Find out the volume of B which will diffuse in the same time in which 150 dm^3 of A will diffuse.

Ans. Given data:

Relative density of gas A $= d_A = 1.00$
Relative density of gas B $= d_B = 1.5$
Volume of gas A diffused $= V_A = 150\ dm^3$

Required:

Volume of gas B diffused $= V_B = ?$

Solution:

According to Graham's law

$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$$

Volume of gases diffused is directly related to their rates of diffusion, so

$$\frac{\text{Volume of gas A diffused}}{\text{Volume of gas B diffused}} = \sqrt{\frac{d_B}{d_A}}$$

$$\frac{150}{V_B} = \sqrt{\frac{1.5}{1}}$$

Take square of both sides

$$\left(\frac{150}{V_B}\right)^2 = \left(\sqrt{\frac{1.5}{1}}\right)^2$$

$$\frac{150}{(V_B)^2} = \frac{1.5}{1}$$

$$(V_B)^2 = \frac{(150)^2}{1.5} = \frac{22500}{1.5} = 15000$$

$$\sqrt{(V_B)^2} = \sqrt{15000}$$

$$\text{V of B} = 122.47\ dm^3$$

Volume of gas B which will diffuse in same time as 150 dm^3 of gas A = 122.47 dm^3

(b) Hydrogen diffuses through a porous plate at a rate of 500 cm^3 per minute at 0°C. What is the rate of diffusion of oxygen through same porous plate at 0°C?

Ans. Given data:

Volume of a gas diffused is directly proportion to its rate of diffusion so V_{H_2} can be written as r_{H_2} = 500 cm^3

Molar mass of H_2 gas = 2 g mol^{-1} = M_{H_2}

Molar mass of O_2 gas = 32 g mol^{-1} = M_{O_2}

Required:

r_{O_2} = ?

Solution:

According to Graham's law.

$$\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}}$$

$$\frac{500}{r_{O_2}} = \sqrt{\frac{32}{2}}$$

$$\frac{500}{r_{O_2}} = \sqrt{16}$$

$$\frac{500}{r_{O_2}} = 4$$

$$r_{O_2} = 125$$

Rate of diffusion of O_2 is 125 cm^3 / min from porous plate where H_2 diffuses at 500 cm^3 / min.

(c) The rate of effusion of an unknown gas A through a pin hole is found to be 0.279 times that of H_2 through same pin hole. Calculate the molar mass of gas A.

Ans. Given data:

Relative rate of effusion of Hydrogen = r_{H_2} = 1.00

Relative rate of effusion of gas A = r_A = 0.279

Molar mass of Hydrogen gas = M_{H_2} = 2 g mol^{-1}

Required:

Molar mass of gas A = M_A = ?

Solution:

According to Graham's law

$$\frac{r_{H_2}}{r_A} = \sqrt{\frac{M_A}{M_{H_2}}}$$

$$\frac{1.0}{0.279} = \sqrt{\frac{M_A}{2}}$$

Take square on both sides.

$$\left(\frac{1.0}{0.279}\right)^2 = \left(\sqrt{\frac{M_A}{2}}\right)^2$$

$$\frac{1}{0.07784} = \frac{M_A}{2}$$

$$M_A = \frac{2}{0.07784} = 25.7\ g\ mol^{-1}$$

Molar mass of gas A = 25.7 g mol^{-1}

Q22. Calculate the number of molecules and the number of atoms in the given amount of each gas.

(a) 20 cm^3 of CH_4 at 0°C and pressure of 700 mm of mercury.

Ans. Given data:

Pressure of CH_4 gas = 700 mm of Hg = $\frac{700}{760}$ = 0.921 atm

= 0.921 atm

Volume of gas = 20 cm^3 = 0.02 dm^3

Temperature = 0°C + 273 = 273 K

R = 0.0821 atm.dm^3.mol^{-1} K^{-1}

Required:

Number of molecules of CH_4 = ?

Number of atoms = ?

Solution:

To calculate the number of molecules or atom first thing is to calculate moles (n)

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{0.921 \times 0.02}{0.0821 \times 273}$$

$$= 8.2 \times 10^{-4}\ mol$$

No. of molecules = No. of moles × N_A

= $8.2 \times 10^{-4} \times 6.02 \times 10^{23}$

= 4.94×10^{20} molecules

As one molecule of CH_4 has atoms = 5

4.94×10^{20} molecules of CH_4 have total atoms = $4.94 \times 10^{20} \times 5$

= 2.47×10^{21} atoms

Total molecules of CH_4 = 4.94×10^{20}

Total atoms in those molecules = 2.47×10^{21} atoms

(b) 1 cm^3 of NH_3 at 100°C and pressure of 1.5 atm.

Ans. Given data:

Volume of gas = V = 1 ml = 1 cm^3

= 0.001 dm^3

Pressure = P = 1.5 atm

Temperature = T = 100°C + 273 = 373 K

R = 0.0821 atm.dm^3.mol^{-1} K^{-1}

Required:

Number of molecules of NH_3 = ?

Total number of atoms = ?

Solution:

Firstly, we will calculate number of moles (n) by using general gas equation

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{1.5 \times 0.001}{0.082 \times 373}$$

$$= 4.89 \times 10^{-5} \text{ moles}$$

No. of molecules $= \text{no. of moles} \times N_A$

$$= 4.89 \times 10^{-5} \times 6.02 \times 10^{23}$$

$$= 2.95 \times 10^{19} \text{ molecules}$$

One molecule of NH_3 contain atoms $= 4$

2.95×10^{19} molecules of NH_3 contain atoms $= 2.95 \times 10^{19} \times 4$

$= 1.18 \times 10^{20}$ atoms

Total molecules $= 2.95 \times 10^{19}$ **molecules**

Total atoms $= 1.18 \times 10^{20}$ **atoms**

Q23. Calculate the masses of 10^{20} molecules of each of H_2, O_2 and CO_2 at STP. What will happen to the masses of these gases, when the temperatures of these gases are increased by 100°C and pressure is decreased by 100 torr.

Ans. Given data:

Molecules of each gas $= 10^{20}$ molecules

Molar mass of H_2 $= 2 \text{ g mol}^{-1}$

Molar mass of O_2 $= 32 \text{ g mol}^{-1}$

Molar mass of CO_2 $= 44 \text{ g mol}^{-1}$

Required:

Mass of H_2 = ?

Mass of O_2 = ?

Mass of CO_2 = ?

Solution:

No. of molecules $= \text{number of moles} \times N_A$

or

$$\text{No. of molecules} = \frac{\text{mass in g}}{\text{Mol mass}} \times N_A$$

Therefore,

$$\text{mass in g} = \frac{\text{Mol. mass} \times \text{number of molecules}}{N_A}$$

(a) Mass in g for H_2 $= \frac{2 \times 10^{20}}{6.02 \times 10^{23}} = 3.32 \times 10^{-4}$ g

(b) Mass in g for O_2 $= \frac{32 \times 10^{20}}{6.02 \times 10^{23}} = 5.31 \times 10^{-3}$ g

(c) Mass in g for CO_2 $= \frac{44 \times 10^{20}}{6.02 \times 10^{23}} = 7.3 \times 10^{-3}$ g

Effect of temperature and pressure: Both temperature and pressure effect the volume and not the mass. Therefore by changing any of these parameters no effect on mass is observed.

Mass of H_2 $= 3.32 \times 10^{-4}$ **g**

Mass of O_2 $= 5.31 \times 10^{-3}$ **g**

Mass of CO_2 $= 7.31 \times 10^{-3}$ **g**

Q24. (a) Two moles of NH_3 are enclosed in a 5 dm³ flask at 27°C. Calculate the pressure exerted by the gases assuming that

(i) Gas behaves ideal.

(ii) Gas behaves like a real gas.

$a = 4.17 \text{ atm dm}^6 \text{ mol}^{-2}$

$b = 0.0371 \text{ dm}^3 \text{ mol}^{-1}$

Ans. Given data:

Number of moles of NH_3 = n = 2 moles

Volume of gas = V = 5 dm³

Temperature = T = 27°C + 273 = 300K

$R = 0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}$

Required:

Pressure = P = ?

When

(i) Gas behave ideally

(ii) Gas behaves like a real gas

(i) Solution:

When gases behave ideally they follow general gas equation i.e.,

$$PV = nRT$$

$$P = \frac{nRT}{V} = 2 \times \frac{0.0821 \times 300}{5}$$

Ideal pressure = P = 9.852 atm

(ii) Solution:

When gases behave non-ideally they follow van der Waal's equation i.e

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$P + \frac{n^2a}{V^2} = \frac{nRT}{(V - nb)}$$

$$P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

$$= \frac{2 \times 0.0821 \times 300}{5 - 2(0.0371)} - \frac{2^2 \times 4.17}{(5)^2}$$

$$= \frac{49.26}{4.9258} - \frac{16.68}{25}$$

Real pressure = 10.01 – 0.6672 = 9.34 atm

Ideal pressure = 9.852 atm

Real pressure = 9.34 atm

(b) Also calculate the amount of pressure lessened due to force of attraction at these conditions of volume and temperature:

Ans. Given data:

As calculated in (a)

Ideal pressure $= P_i = 9.852$ atm

Real pressure $= P = 9.34$ atm

Required:

Pressure lessened $= P' = ?$

Solution:

$P_{ideal} - P_{real} = P'$

$P' = 9.852 - 9.34$

$P' = 0.512$ atm

(c) Do you expect the same decreases of pressure for two moles of NH_3 having a volume of 40 dm^3 and temperature of 27°C.

Ans. Given data:

Moles of NH_3 $= n = 2$ moles

Temperature $= T = 27°C = 300$ K

Volume of gas $= V = 40$ dm^3

R $= 0.0821$ atm dm^3 mol^{-1} K^{-1}

Required:

(i) $P_{ideal} = P = ?$

(ii) $P_{real} = P = ?$

(iii) $P' = ?$

Solution:

(i) Ideal pressure:

$PV = nRT$

$$P = \frac{nRT}{V}$$

$$= \frac{2 \times 0.0821 \times 300}{40}$$

$= 1.23$ atm

(ii) Real pressure:

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

By applying values

$$P = \frac{2 \times 0.082 \times 300}{40 - 2(0.0371)} - \frac{4 \times 4.17}{(40)^2}$$

$$P = \frac{49.26}{39.92} - \frac{16.68}{1600}$$

$P = 1.233 - 0.010425$

$P = 1.22$ atm

(iii) $P' = P_{ideal} - P_{real}$

$= 1.23 - 1.22 = 0.01$ atm

We can compare the lessened pressures in both cases and find that greater volume of 40 is dm^3 in more suitable for ideal behaviour as compare to 5 dm^3. As greater volume lessened the forces of attraction.

Lessened pressure in first case $= 0.512$ atm

Lessened pressure in second case $= 0.01$ atm

SOLVED EXAMPLES

Example (1)

A gas having a volume of 10dm^3 is enclosed in a vessel at 0°C and the pressure is 2.5 atmospheres. This gas is allowed to expand until the new pressure is 2 atmospheres. What will be the new volume of this gas, if the temperature is maintained at 273K.

Ans. Given Data

Initial volume of gas $= V_1 = 10$dm^3

Initial temperature $= T_1 = 0°C + 273 = 273$K

Initial pressure $= P_1 = 2.5$atm

Final pressure $= P_2 = 2$atm

Final temperature $= T_2 = 273$K

Required

Final volume $= V_2 = ?$

Solution

Since the temperature is constant $(T_1 = T_2)$.

Boyle's law is applicable

$P_1V_1 = P_2V_2$ (at content T and n)

$$V_2 = \frac{P_1V_1}{P_2}$$

$$V_2 = \frac{2.5 \times 10\text{dm}^3}{2\text{atm}} = 12.5\text{dm}^3$$

∴ **Volume of the gas = 12.5dm^3 Answer**

Example (2)

250cm^3 of Hydrogen is cooled from 127°C to -27°C by maintaining the pressure constant. Calculate new volume of the gas at low temperature.

Ans. Given Data:

Initial Volume $= V_1 = 250$cm^3 $= 0.25$dm^3

Initial Temperature $= T_1 = 127°C + 273K = 400K$

Final Temperature $= T_2 = -27°C + 273K = 2461K$

Required

Final volume $= V_2 = ?$

Solution:

According to Charles's law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$ (at constant P and n)

$$V_2 \frac{V_1T_2}{T_1}$$

$$V_2 = \frac{0.25\text{dm}^3 \times 246\text{K}}{400\text{K}} = 0.153\text{dm}^3 = 153\text{cm}^3$$

Volume of the gas at low temperature = 153cm^3 Answer

Example (3)

A sample of Nitrogen gas is enclosed in a vessel of volume 380cm³ at 120°C and pressure of 101325Nm⁻². This gas is transferred to a 10dm³ flask and cooled to 27°C. Calculate the pressure in Nm⁻² exerted by the gas at 27°C.

Ans. **Given Data**

Initial pressure = P_1 = 101325Nm^{-2}

Initial volume = V_1 = 380cm^3 = $\frac{380}{1000}$ = 0.380dm^3

Initial temperature = T^1 = 120°C + 273K = 393K

Final temperature = T_2 = 27 + 273K + 300K

Final volume = V_2 = 10dm^3

Required:

Final pressure = ?

Solution

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{V_2}$$

$$P_2 = \frac{101325Nm^{-2} \times 0.38dm^3 \times 300K}{393K \times 10dm^3}$$

$$= 2938Nm^{-2}$$

Pressure = 2938Nm^{-2} Answer

Example (4)

Calculate the density of $CH_{4(g)}$ at 0°C and 1atm pressure. What will happen to the density if (a) temperature is increased to 27°C, (b) the pressure is increased to 2atm at 0°C.

Ans. **Given Data**

Temperature of the gas = T = 0°C + 273K = 273K

Pressure = P = 1atm

Molecular Mass of CH_4 = M = 12 + 4 = 16 g mol^{-1}

Gas constant = R = 0.0821 dm^3 atm K^{-1} mol^{-1}

Required

Density of the gas = d = ?

Solution: **Formula**

$$d = \frac{PM}{RT}$$

Putting values

$$d = \frac{1atm\ 16g\ mol^{-1}}{0.0821atm\ dm^3\ K^{-1}\ mol^{-1} \times 273K}$$

Simplifying the units

$$d = \frac{1 \times 16}{0.0821 \times 273} gdm^{-3}$$

$$= 0.7138gdm^{-3}$$

d = 0.7138gdm^{-3} Answer

It means that under the given condition 1dm^3 of CH_4 gas has a mass of 0.7138gdm^{-3}.

(b) **Given Data:**

Temperature = T = 0°C + 273 + 273K

Pressure = P = 2atm

Required

Density = d = ?

Solution

$$d = \frac{PM}{RT} = \frac{2atm \times 16g\ mol^{-1}}{0.0821atm\ dm^3 . K^{-1}\ mol^{-1} \times 273K}$$

d = 1.427gdm^{-3}

Density = d = 1.427gdm^{-3}

The increase of pressure has increased the density of CH_4. The density has almost doubled by doubling the pressure the Reason is that increase of pressure make the molecules to come close to each other

Example (5)

Calculate mass of 1dm³ of NH_3 gas at 30°C and 1000mm Hg pressure, considering that NH_3 is behaving ideally.

Ans. **Given Data:**

Pressure = P = 1000mmHg = $\frac{1000}{760}$ = 1.315atm

Volume = V = 1dm^3

Temperature = T = 30°C + 273 = 303K

Molar mass = M = 17g/mol

Required

Mass of the gas = m = ?

Solution

Formula $PV = \frac{m}{M}RT$

R = 0.0821atm dm^3 K^{-1} mol^{-1}

Putting values along with units

$$\text{Mass of } NH_3 = m = \frac{1.315atm \times 1dm^3 atm \times 17g\ mol^{-1}}{0.0821atm\ dm^3\ K^{-1}\ mol^{-1} \times 303K}$$

Simplifying the units

$$\text{Mass of } NH_3 = \frac{1.315 \times 1 \times 17}{0.0821 \times 303} = 0.907g$$

Mass of NH_3 = 0.907g Answer

Example (6)

There is a mixture of H_2, He and CH_4 occupying a vessel of volume 13dm³ at 37°C and pressure is 1atm. The masses of H_2 and He are 0.8g and 0.12g respectively. Calculate the partial pressures in torr of each gas in the mixture.

Ans. **Given Data:**

Volume of the mixture of gases = 13dm^3

Temperature of the mixture = 37 + 273 = 310K

Pressure of the mixture = 1atm

Mass of H_2 = 0.8g

Mass of He = 0.12g

Required:

Partial pressure of H_2 = pH_2 = ?

Partial pressure of He = pHe = ?

Partial pressure of CH_4 = pCH_4 = ?

Solution:

First calculate the total number of moles present in the mixture of gases by applying the general gas equation.

Since

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

Putting values along with the units and simplifying

$$n = \frac{1\ atm \times 13\ dm^3}{0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1} \times 310K}$$

$$= 0.51\ moles$$

Since, the total number of moles of H_2, He and CH_4 = 0.51moles

Number of moles of H_2 $= \frac{\text{Mass of } H_2}{\text{Molar mass of } H_2} = \frac{0.8g}{2.0g\ mole^{-1}} = 0.40mole$

Number of moles of He $= \frac{\text{Mass of He}}{\text{Molar mass of He}} = \frac{0.12g}{4g\ mol^{-1}} = 0.03moles$

Number of moles of CH_4 $= 0.51 - 0.4 - 0.03 = 0.084$

Mole fraction of H_2 (X_{H2}) $= \frac{\text{number of moles of } H_2}{\text{total number of moles}} = \frac{0.40}{0.51} = 0.784$

Mole fraction of He (X_{He}) $= \frac{\text{number of moles of He}}{\text{total number of moles}} = \frac{0.03}{0.51} = 0.058$

Mole fraction of CH_4 (X_{CH4}) $= \frac{\text{number of moles of } CH_4}{\text{total number of moles}} = \frac{0.084}{0.51} = 0.164$

(Being a ratio mole fraction has no units)

Partial pressure of H_2 (pH_2) $= X_{H2}\ P$

$= 0.776 \times 1.00 = 0.776$ atm

$= 0.766 \times 760 = 589.76$ torr

Partial pressure of H_e (pHe) $= X_{He}\ P$

$= 0.058 \times 1.00 = 0.058$ atm

$= 0.058 \times 760 = 44.08$ torr

Partial pressure of CH_4 (pCH_4) $= X_{CH4}\ P$

$= 0.164 \times 1.00 = 0.164$ atm

$= 0.164 \times 760 = 124.64$mm of Hg **Answer**

Example (7)

250cm³ of the sample of Hydrogen effuse four times as rapidly as 250cm³ of an unknown gas. Calculate the molar mass of unknown gas.

Ans. **Given Data**

Rate of effusion of unknown gas (r_x) = 1

Rate of effusion of hydrogen gas = r_{H2} = 4

Molar mass of hydrogen gas = M_{H2} = 2g/mol⁻¹

Required:

Molar mass of unknown gas = M_x = ?

Solution: **Formula**

$$\frac{r_{H2}}{r_x} = \sqrt{\frac{M_x}{M_{H2}}}$$

Putting the value

$$\frac{4}{1} = \sqrt{\frac{M_x}{2}}$$

Taking square on both sides

$$\left(\frac{4}{1}\right)^2 = \left(\sqrt{\frac{M_x}{2}}\right)^2$$

$$\frac{16}{1} = \frac{M_x}{2}$$

$$M_x = 16 \times 2 = 32gmol^{-1}$$

Molar Mass of unknown gas = 32gmol⁻¹ Answer

Example (8)

One mole of methane gas is maintained at 300K. Its volume is 250cm³. Calculate pressure exerted by the gas under the following condition

(i) When the gas is ideal **(ii) When the gas is non-ideal**

a = 2.253atm dm⁶ mol⁻² b = 0.0428dm³ mol⁻¹

Ans. **Given Data**

Mole of CH_4 = n = 1 mole

Volume = V = 250cm³ = 0.25dm³ [1dm³ = 1000cm³]

Temperature = T = 300K

Gas constant = R = 0.0821dm³ atmK⁻¹ mol⁻¹

a = 2.253atm dm⁶ mol⁻²

b = 0.0428dm³ mol⁻¹

Required

Pressure exerted by the gas

(i) When the gas is ideal

(ii) When the gas is non-ideal

Solution

(i) **When the gas is ideal, general gas is applied.**

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$= \frac{1mole \times 0.0821dm^3 atm\ K^{-1}\ mole^{-1} \times 300K}{0.25dm^3}$$

P = **98.5atm** Answer

If CH_4 gas would have been ideal, under the given condition, 98.5atm. pressure would have been exerted

(ii) **When the gas is behaving as non-ideal, van der Waals's equation.**

$$\left(P + \frac{n^2a}{v^2}\right)(V - nb) = nRT$$

By rearranging the equation and taking the pressure on L.H.S

$$\left(P + \frac{n^2a}{v^2}\right) = \frac{nRT}{V - nb}$$

or $$P = \frac{nRT}{V - nb} - \frac{n^2a}{v^2}$$

Putting the values

$$P = \frac{1 \times 0.0821 \times 300}{0.25 - 1\,(0.0428)} - = \frac{24.63}{0.207} - \frac{2.253}{0.0625}$$

$P = 118.985 - 36.048 = 82.85\,atm$

In non ideal situation the pressure has lessened up to

$= 98.5 - 82.85 = 15.65\,atm$

Additional Questions

Q. Atmospheric pressure on the top of Mount Everest is 323 mm Hg. Convert this value to Pascals and to atmospheres.

Ans.

$$265\,mm\,Hg \times \frac{101.325\ Pa}{760\,mm\,Hg} = 3.53 \times 10^4\ Pa$$

$$265\,mm\,Hg \times \frac{1atm}{760\,mm\,Hg} = 0.349\,atm$$

Q. Ammonia gas has high critical temperature than H_2 gas. Justify the statement.

Ans. *Ammonia is a polar gas in which molecules experience strong intermolecular forces between them. These strong forces become dominant at even higher temperature by applying pressure and gas is converted into liquid. Hence, critical temperature is high for NH_3.*

H_2 is a non-polar gas experiencing weak intermolecular forces. By applying the pressure, these weak forces can become strong enough at very low temperature where gas can be converted into liquid. Hence, critical temperature is low.

Important Previous Board Questions

- **Q.** *Justify that $1cm^3$ of H_2 and $1cm^3$ of CH_4 at STP will have same number of molecules although one molecule of CH_4 is 8 times heavier than that of hydrogen.*
- **Q.** *Gases deviate more from the general gas equation at 0°C and deviate to less extent at 100°C. Why?*
- **Q.** *Why the volume correction is done by van der Waals?*
- **Q.** *Greater the temperature of the gas, closer the straight line of P versus 1/V to the pressure axis. Justify it.*
- **Q.** *Why gases do not settle down in a vessel?*
- **Q.** *Why reguler air cannot be used in divers tank?*
- **Q.** *-273.16°C is regarded as the lowest possible temperature. Justify it.*
- **Q.** *Gases deviate from ideal behaviour more significantly at high pressure, why?*
- **Q.** *Density of a gas is related to pressure and temperature of the gas. Justify it.*
- **Q.** *What is Compressibility factor? What is its value for an Ideal Gas?*
- **Q.** *What is the relation between kinetic energy, temperature and state of matter?*
- **Q.** *One mole of H_2 and O_2 have same number of molecules. Why?*
- **Q.** *What is elastic collision? Give an example.*

For Answers study Scholar's CHEMISTRY (Objective) XI

Chapter 4

LIQUIDS AND SOLIDS

Differentiate between Intramolecular Forces and Intermolecular Forces

Intramolecular forces	Intermolecular forces
• Those forces which are present within the molecules between atoms are called intramolecular forces.	• Those forces which are present between two molecules are called intermolecular forces
• Nature of substance is determined by intramolecular forces.	• State of a substance (solid, liquid and gas) is determined by intermolecular forces.
• Chemical properties of a substance are related to its intramolecular forces.	• The physical properties of a substance are related to its intermolecular forces.
• These are comparatively strong forces.	• These are relatively weak forces
Examples (i) Covalent bond (ii) Ionic bond (iii) Coordinate covalent bond	**Examples** (i) Dipole-dipole forces (ii) Dipole-induced dipole forces (iii) London dispersion forces (iv) Hydrogen bonding

- **Covalent bonds act between atoms.**
- **Ionic bonds act between ions (cations and anions).**
- **Metallic bonds act between positive ions and electrons.**
- **Hydrogen bonds act between polar molecules.**
- **dipole-dipole interactions act between polar molecules.**
- **van der Waals's forces act between all molecules.**

Dipole-dipole Forces

"The attractive forces present between the positive end of one molecule and the negative end of another polar molecule are called dipole-dipole forces."

Dipole: Partial separation of charges on a bond between two atoms or a polar molecule is simply called a dipole

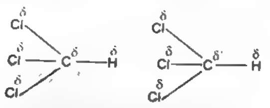
Examples:

(i) **In HCl molecule,** both atoms differ in electronegativity. Chlorine being more electronegative, develops the partial negative charge and hydrogen develops the partial positive charge. So, whenever, molecules are close to each other, they tend to line up.

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl} \cdots\cdots \overset{\delta^+}{H} - \overset{\delta^-}{Cl} \cdots\cdots \overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

However, thermal energy causes the molecules not to have a perfect alignment.

(ii) **In $CHCl_3$ molecule,** dipole dipole forces are present between hydrogen atoms of one molecule and chlorine atoms of other molecule.



Dipole - dipole forces present in HCl molecules and chloroform ($CHCl_3$) molecules.

Factors affecting dipole-dipole forces

(i) Electronegativity difference

Greater the electronegativity difference between bonded atoms, greater will be the dipole-dipole forces.

(ii) Intermolecular distance

The distances between molecules in the gaseous phase are greater so these forces are very weak in this phase In liquids, these forces are reasonably strong.

Important points

- These forces are present between polar molecules.
- These forces are approximately 1% as effective as a covalent bond.
- Greater the strength of these dipole-dipole forces, greater are the values of thermodynamic parameters like melting points, boiling points heats of vapourization and heats of sublimation.

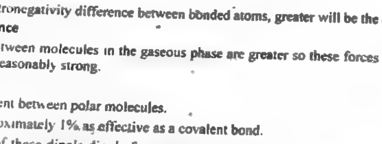
Dipole-induced Dipole Forces (Debye Forces)

"The attractive forces present between permanent dipole and induced dipole are called dipole- induced dipole forces or Debye forces."

e.g. in a mixture of HCl and Ne, Debye forces are present between molecules.

Explanation

Sometimes, we have a mixture of substances containing polar and non-polar molecules. The positive end of polar molecule attracts the mobile electrons of the nearby non-polar molecule. In this way, polarity is induced in non-polar molecule and both molecules become dipoles. These forces are called induced dipole or Debye forces. These forces are present in a mixture of polar and non-polar molecules.



Fig(4.2) Dipole-induced dipole interactions

London Dispersion Forces (Instantaneous Dipole–Induced Dipole Forces)

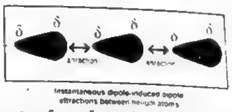
"The attractive forces between the temporary dipole in one molecule and temporary induced dipole in an adjacent molecule are called London dispersion forces."

Discovery

A German physicist Fritz London in 1930 offered a simple explanation for these weak attractive forces between non-polar molecules

Explanation

In a gas (say He), the electrons of one atom influence the moving electrons of the other atom. Electrons repel each other and they tend to stay as far apart as possible. When the electrons of one atom come close to the electrons of other atom, they are pushed away from each other. In this way, a temporary dipole is created in the atom. The result is that, at any moment, the electron density of the atom is no more symmetrical. It has more negative charge on one side than on the other At that particular instant, the atom becomes a dipole. This is called instantaneous dipole. This instantaneous dipole then disturbs the electronic cloud of the other nearby atom. So, a dipole is induced in the second atom.



Instantaneous dipole-induced dipole attractions between helium atoms

This is called induced dipole. The momentary force of attraction created between instantaneous dipole and the induced dipole is called instantaneous dipole-induced dipole interaction or London force

Important points

- It is a very short-lived attraction because the electrons keep moving
- This movement of electrons causes the dipoles to vanish as quickly as they are formed.
- London forces are present in all types of molecules whether polar or non-polar, but they are very significant for non-polar molecules like Cl_2, H_2 and noble gases (helium, neon, etc.)

Factors Affecting the London Forces

(i) Size of electronic cloud

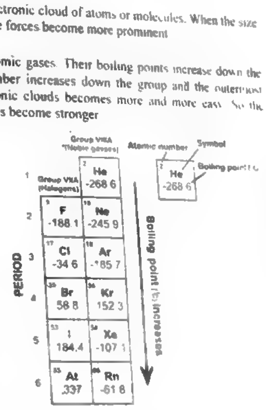
The strength of London forces depends upon the size of the electronic cloud of atoms or molecules. When the size of the atom or molecule is large then dispersion becomes easy and these forces become more prominent

Group VIII A (Noble Gases)

The elements of the zero group in the periodic table are all mono-atomic gases. Their boiling points increase down the group from helium (–268.6°C) to radon (–61.8°C). The atomic number increases down the group and the outermost electrons move away from the nuclei. The dispersion of the electronic clouds becomes more and more easy. So the polarizability of these atoms go on increasing as a result, London forces become stronger

Group VII A (Halogens)

All the halogens are non-polar diatomic molecules, but there is a big difference in their physical state at room temperature. Fluorine is a gas and boils at –188.1°C while iodine is a solid at room temperature which boils at +184.4°C. The polarizability of iodine molecule is much greater than that of fluorine.



(ii) Number of atoms in a molecule:

Greater the number of atoms in a molecule, greater is its polarizability and hence stronger will be London forces.

- **Saturated hydrocarbons (Alkanes)**

Compare the length of the chain for ethane (C_2H_6) and hexane (C_6H_{14}). They have the boiling points –88.6°C and 68.7°C respectively. This means that a molecule with a large chain length experiences stronger attractive forces. The reason is that longer molecules have more places along its length where they can be attracted to other molecules.

Boiling points and physical states of some hydrocarbons

Name	B.P °C(1atm)	Physical state at STP	Name	B.P °C(1atm)	Physical state at STP
Methane	-161.5	Gas	Pentane	36.1	Liquid
Ethane	-88.6	Gas	Hexane	68.7	Liquid
Propane	-42.1	Gas	Decane	174.1	Liquid
Butane	-0.5	Gas	Isodecane	327	Solid

It is very interesting to know that with the increasing molecular mass of these hydrocarbons, they change from gaseous to liquid and then finally become solids.

Q. Why ethane (C_2H_6) is a gas while hexane (C_6H_{14}) is a liquid?

Ans: The physical state of a substance depends upon strength of inter molecular forces. Alkanes are non polar and have weak London forces in them. Hexane has large chain length. So it experiences stronger attractive forces. Thus it exists in liquid state. On the other hand ethane exists in a gaseous state because it experiences weak London forces

Hydrogen Bonding

"The electrostatic force of attraction between hydrogen atom (bonded to a small highly electronegative atom) and the electronegative atom (F, O, N) of another molecule is called hydrogen bonding."

- The electronegative atoms responsible for creating hydrogen bonding are fluorine, oxygen, nitrogen and rarely chlorine. The strength of hydrogen bond is generally twenty times less than that of a covalent bond.

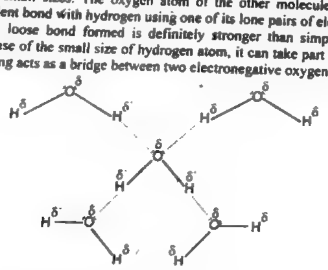
Examples:

(i) Water (H_2O)

In case of H_2O, oxygen is a more electronegative element as compared to hydrogen, so water is a polar molecule. Hence, there will be dipole-dipole interactions between partial positively charged hydrogen and partially negatively charged oxygen atoms. Actually, hydrogen bonding is something more than dipole-dipole interaction. Firstly, oxygen atom has two lone pairs. Secondly hydrogen has sufficient partial positive charge. Both the hydrogen atoms of water molecule create strong electrical field due to their small sizes. The oxygen atom of the other molecule links to form a coordinate covalent bond with hydrogen using one of its lone pairs of electrons.

Thus, loose bond formed is definitely stronger than simple dipole-dipole interaction. Because of the small size of hydrogen atom, it can take part in this type of bonding. This bonding acts as a bridge between two electronegative oxygen atoms.

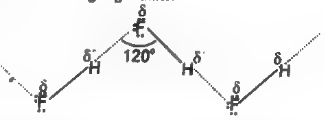
A hydrogen bond is a comparatively strong intermolecular attraction between:
- an electron deficient hydrogen atom, $H^{\delta+}$, on one molecule
- a lone pair of electrons on a highly electronegative atom of F, O or N on another molecule.



Hydrogen bonding in water

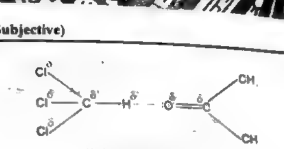
(ii) Hydrofluoric acid (HF)

The molecules of HF join with each other in a zig-zag manner.



(iii) Chloroform and acetone

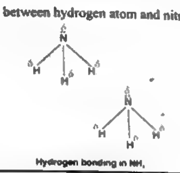
In case of chloroform, three chlorine atoms are responsible for H-bonding with other molecules. These atoms deprive the carbon atom of its electrons and the partial positively charged hydrogen can form a strong hydrogen bond with oxygen atom of acetone.



Hydrogen bonding between chloroform and acetone

(iv) Ammonia (NH_3)

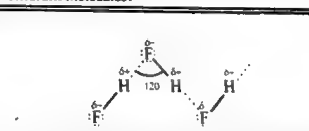
In ammonia we also observe hydrogen bond between hydrogen atom and nitrogen atom



Hydrogen bonding in NH_3

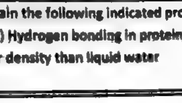
Q. Why HF is a weaker acid as compared to HCl, HBr and HI?

Ans. The strength of an acid depends upon the extent of its ionization. The low acidic strength of HF molecule as compared to HCl, HBr and HI is due to the strong hydrogen bonding in HF molecules. As the partial positively charged hydrogen is entrapped between two highly electronegative atoms so this acid do not ionizes completely in water and hence HF becomes a weak acid.



(i) In the hydrogen bonded structure of HF which is the stronger bond, the shorter covalent bond or the longer hydrogen bond between different molecules?

Ans. **Structure of HF:**



(i) The intermolecular forces between the molecules of HF are hydrogen bonding.

(ii) The intramolecular forces within the molecule of HF are covalent bond.

Since, the strength of hydrogen bond is generally twenty times less than that of a covalent bond. Therefore, covalent bond is a stronger bond than the hydrogen bond between the molecules of HF

Q.12 How does hydrogen bonding explain the following indicated properties of the substances?

(i) Structure of DNA **(ii) Hydrogen bonding in proteins**

(iii) Formation of ice and its lesser density than liquid water

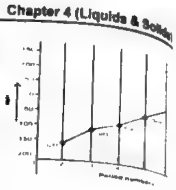
(iv) Solubilities of compounds

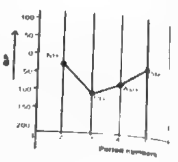
Properties and Applications of Compounds Containing Hydrogen Bonding

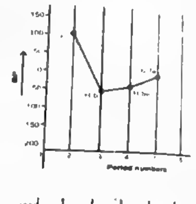
1. Thermodynamic properties of covalent hydrides:

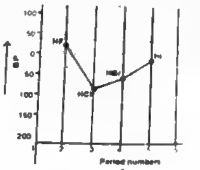
Hydrogen bonding (exists in the compounds) influences the physical properties like melting and boiling points. Let us compare the physical properties of hydrides of group IV-A, V-A, VI-A, and VII-A. The graphs are plotted between the period number of periodic table on X-axis and boiling points in centigrade on Y-axis.

- Boiling points of hydrides of IV-A group have low boiling points as compared to those of group V-A, VI-A and VII-A. The reason is that these elements are least electronegative. CH_4 has lowest boiling point because it is a very small molecule and its polarizability is least.
- When we consider the hydrides of group V-A, VI-A and VII-A, then NH_3, H_2O and HF show maximum boiling points in the respective series. The reason is the **enhanced electronegative character of N, O and F**. That is why water is liquid at room temperature but H_2S and H_2Se are gases.
- The boiling point of water (100°C) seems to be more affected by hydrogen bonding than that of HF (19.9°C). Fluorine is more electronegative than oxygen. So, we should expect hydrogen bonding in HF to be stronger than that in water and as a result the boiling point of HF should be higher than that of H_2O. However, it is lower and the reason is that fluorine atom can make only one hydrogen bond with electropositive hydrogen of a neighboring molecule. Water can form two hydrogen bonds per molecule as it has two hydrogen atoms and two lone pairs on oxygen atom. Ammonia can form only one hydrogen bond per molecule as it has only one lone pair.
- The boiling point of HBr is slightly higher than that of HCl. It means that chlorine is electronegative enough to form a hydrogen bond. Sometimes it is thought that HCl has a strong dipole-dipole forces but in reality, it is a borderline case.
- **The hydrides of fourth period**, i.e. GeH_4, ASH_3, H_2Se, HBr show greater boiling points than those of third period due to greater size and enhanced polarizabilities.





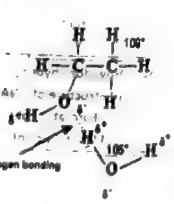




Hydrides	B.P (°C)	Hydrides	B.P (°C)
CH_4	-164	H_2O	100
SiH_4	1*2	H_2S	-61
GeH_4	-88	H_2Se	-42
SnH_4	-52	H_2Te	-2
NH_3	-33.4	HF	19.9
PH_3	-88	HCl	-85
AsH_3	-55	HBr	-67
SbH_3	17	HI	-36

2. Solubility of Hydrogen Bonded Molecules

- Water is the best example of hydrogen bonded system. Ethyl alcohol (C_2H_5OH) also has the tendency to form hydrogen bonds. So ethyl alcohol can dissolve in water because both can form hydrogen bonds with each other.
- Carboxylic acids are soluble in water, if their sizes are small. They form hydrogen bond with water molecules and thus dissolve.
- Hydrocarbons are not soluble in water at all, because they are non-polar compounds and there are no chances of hydrogen bonding between water and hydrocarbon molecules.



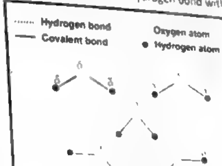
Hydrogen bonding

(iii) Water and ethanol can mix easily and in all proportions:

Ans. Water and ethanol (C_2H_5OH) both molecules have –OH groups so both compounds show hydrogen bonding. As like dissolves like, so ethanol can mix in water in all proportions due to the formation of hydrogen bond with each other. Hydrogen bonding between water and ethanol is.

3. Structure of Ice

The molecules of water have tetrahedral structure. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron. In the liquid state, water molecules are extensively associated with each other and these associations break and are reformed because the molecules of water are mobile.



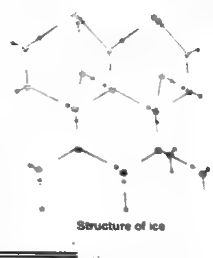
Structure of liquid water

- **Density of ice**

When the temperature of water is decreased and ice is formed then molecules become more regular and this regularity extends throughout the whole structure. Empty spaces are created in the structure. That is why when water freezes it occupies 9% more space and its density decreases. The result is that ice floats on water.

- **Diamond like structure**

The structure of ice is just like that of a diamond because each atom of carbon in diamond is at the centre of tetrahedron just like the oxygen of water molecule in ice.



Structure of ice

- **Aquatic life under the ice**

The lower density of ice than liquid water at 0°C causes water in ponds and lakes to freeze from surface to the downward direction. Water attains the temperature of 4°C by the fall of temperature in the surrounding. As the outer atmosphere becomes further cold, the water at the surface becomes less dense. This less dense water below 4°C stays on the top of slightly warm water underneath. A stage reaches when it freezes. This layer of ice insulates the water underneath for further heat loss. Fish and plants survive under this blanket of ice for months. In short we can say **"The pattern of life for plants and animals would have been totally different in the absence of hydrogen bonding in water."**

(ii) In a very cold winter the fish in garden ponds owe their lives due to hydrogen bonding.

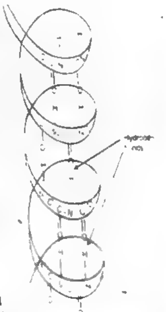
Ans. When water freezes below 0°C, the ice formed stays at the surface due to its lesser density than water. When a compact layer of ice is formed on the surface, it serves as an insulator and prevents the further heat loss from water below it. As a result of that water below this layer of ice exists as a liquid at 4°C. At this temperature of liquid water, fish and plants can survive easily below frozen water. This is how fish and plants can survive under frozen water.

4. Cleansing Action of Soaps and Detergents

The cleansing action of soaps and detergents is due to hydrogen bonding. Reason is that polar parts of their molecules are water soluble (hydrophilic) due to hydrogen bonding and the non-polar parts remain outside water because they are alkyl or benzyl portions and are insoluble in water (hydrophobic).

5. Hydrogen Bonding in Biological Compounds and Food materials

Hydrogen bonding exists in the molecules of living system. Proteins are the important part of living organisms. Fibres like those found in the hair, silk and muscles consist of



Hydrogen bonding in protein

long chains of amino acids These long chains are coiled about one another in a spiral This spiral is called a helix Such a helix may either be right handed or left handed.

- **H- bonding in proteins**

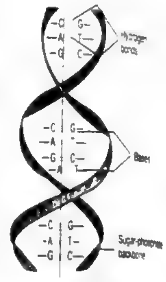
In the case of right handed helix the groups like >NH and >C = 0 are vertically adjacent to one another and they are linked together by hydrogen bonds. These H-bonds link one spiral to the other X-rays analysis has shown that on the average there are 27 amino acid units for each turn of the helix

- **Hydrogen bonding in DNA**

There are two spiral chains in DNA (Deoxyribonucleic acid) which are coiled about each other on a common axis In this way, they give a double helix. This is 18-20Å in diameter They are linked together by H-bonding between their sub-units.

- **H-bonding in carbohydrates**

The food materials like carbohydrates include glucose, fructose and sucrose. They all have –OH groups due to which hydrogen bonding is present.



Hydrogen bonding in DNA double helix

6. Hydrogen Bonding in Paints, Dyes and Textile Materials

One of the most important properties of paints and dyes is their adhesive action. This property is developed due to hydrogen bonding. Similar type of hydrogen bonding makes glue and honey as sticky substances.

Hydrogen bonding is very important in thread making materials like cotton, silk and synthetic fibres for clothing. This hydrogen bonding is responsible for their rigidity and the tensile strength.

Q4a. What type of intermolecular forces will dominate in following liquids?

Ans. **(i) Ammonia, NH_3:** Hydrogen bonding.

(ii) Octane, C_8H_{18}: London dispersion forces.

(iii) Argon, Ar: London dispersion forces.

(iv) Propanone, CH_3COCH_3: Dipole-dipole forces.

(v) Methanol, CH_3OH: Hydrogen bonding.

(b) Propanone (CH_3COCH_3), propanol ($CH_3CH_2CH_2OH$) and butane ($CH_3CH_2CH_2CH_3$) have very similar relative molecular masses. List them in the expected order of increasing boiling points. Explain your answer.

Ans. **Boiling point**

"The temperature at which the vapour pressure of a liquid becomes equal to external pressure is called boiling point of that liquid."

Order of boiling points is

Butane < Propanone < Propanol

(i) Butane is non-polar and it has London dispersion forces.

(ii) Propanone has dipole-dipole forces.

(iii) Propanol has hydrogen bonding

The strongest intermolecular forces are hydrogen bonding and weakest are London forces, so order of boiling points is same as given above.

Q. 5(iv) The origin of the intermolecular forces in water.

Ans. A water molecule contains two hydrogen atoms and one oxygen atom. Oxygen is more electronegative as compared to hydrogen, so water is a polar molecule. Hence there will be dipole-dipole interactions between partially positively charged hydrogen atoms and partially negatively charged oxygen atoms. Oxygen atom has

two lone pairs and hydrogen has sufficiently partial positive charge. Both the hydrogen atoms of water molecule create strong electrical field due to their small sizes The oxygen atom of the other molecule links to form a coordinate covalent bond with hydrogen using one of its lone pairs of electrons.

Thus loose bond formed is definitely stronger than simple dipole-dipole interactions and this interaction is called hydrogen bonding.

EVAPORATION

"The spontaneous change of a liquid into its vapours at the surface of liquid at a given temperature is called evaporation"

Characteristics

(i) Surface phenomenon

The molecules of liquid are not motionless. The energy of molecules is not equally distributed The molecules which have low kinetic energy move slowly while others with high kinetic energy move faster. If one of the high speed molecules reaches the surface it may escape the attractions of its neighboring molecules and leaves the bulk of the liquid

(ii) Endothermic process

As energy is required for evaporation which is absorbed from surrounding, so it is an endothermic process

(iii) Continues at all temperature

The process of evaporation continues at all temperatures and liquid continuously changes in vapours spontaneously.

(iv) Cooling process

Evaporation causes cooling. The reason is that high energy molecules leave the liquid and low energy molecules left behind, the temperature of liquid falls and heat moves from surrounding to liquid and then the temperature of the surrounding also falls.

Factors Affecting Rate of Evaporation

The factors that change the speed at which liquid evaporates are .

1. **Nature of liquid**
   The weaker the intermolecular attractive forces in the liquid, the more rapidly evaporation occurs For example, dimethyl ether evaporates at much faster than ethyl alcohol. A liquid which evaporate more readily is described as being the more volatile.
2. **Temperature:**
   The rate of evaporation increases with increase in temperature. At higher temperature the fraction of molecules having sufficient kinetic energy to escape from the surface increases. This results in the in increase in the rate of evaporation The figure provides the graphic explanation for this behaviour.
3. **Surface area of the liquid:**
   Evaporation is a surface phenomenon. The high energy molecules from the liquid can go into gas phase only through surface. Therefore, greater the surface area of the liquid, the greater is the rate of evaporation

Heat of evaporation:

The quantity of heat required to evaporate a given liquid at constant temperature is defined as the heat of evaporation or vaporisation . The quantity of heat depends upon the strength of the forces of attraction between the molecules in the liquid. Water has a relatively high heat of vaporisation because of the presence of strong attractive forces When one mole of water is completely vaporised at 25°C , it absorbs 44.1 kJ of energy from its surroundings.

$$H_2O_{(l)} + 44.1\ kJ \longrightarrow H_2O_{(g)}$$

The molar heat of vaporisation of water at 25° C is thus 44.1 kJ.

(f) Evaporation causes cooling

Ans. The molecules of a liquid are not motionless. The energy of molecules is not equally distributed Evaporation causes cooling, because when high energy molecules leave the liquid and low energy molecules are left behind, the temperature of liquid falls and heat moves from the surrounding to the liquid and then the temperature of the surrounding also falls. That is why, evaporation causes a cooling effect.

(iii) Evaporation takes place at all temperatures.

Ans. Evaporation:

The spontaneous change of a liquid into its vapours at all temperatures, is called evaporation

1- Rate of evaporation is directly proportional to temperature. At high temperature, the kinetic energy of the molecules increases, so evaporation also increases.

2- At low temperature, the kinetic energy of molecules is less, so rate of evaporation slows down. Thus evaporation continues at all temperatures whether low or high

(iv) Earthenware vessels keep water cool:

Ans. Earthenware vessels are porous. Water rises through these pores by capillary action and evaporates at the surface of the vessel. Remaining over water has low energy molecules so its temperature drops. Further, these earthenware vessels are insulators and do not allow the heat to move in them and hence, water remains cool in earthenware vessels.

(v) One feels sense of cooling under the fan after bath.

Ans. Evaporation is a cooling process and speed of air increases the rate of evaporation. After bath, a thin layer of water is formed on body. When one sits under the fan, the water gets energy from body and evaporates. Increase in the rate of evaporation is facilitated by speed of air. As a result, one feels sense of cooling due to decrease in body temperature.

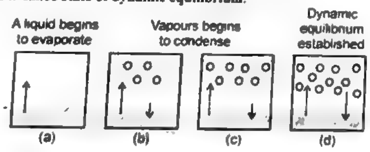
VAPOUR PRESSURE

"The pressure exerted by the vapours of a liquid in equilibrium with the liquid at a given temperature is called vapour pressure."

$$\textbf{Liquid} \xrightleftharpoons{\text{Dynamic equilibrium}} \textbf{Vapours}$$

Explanation

When the molecules of a liquid leave the open surface, they are mixed up with air above the liquid. If the vessel is open, these molecules go on leaving the surface. But if we close the system, the molecules of liquid start gathering above the surface. These molecules not only collide with the walls of container but also with the surface of the liquid as well. There are chances that these molecules are recaptured by surface of liquid. This process is called condensation. The two processes i.e. evaporation and condensation continue till a stage reaches when the rate of evaporation becomes equal to the rate of condensation. This is called **state of dynamic equilibrium**.



Evaporation of a liquid and establishment of dynamic equilibrium between liquid and its vapours.

The number of molecules leaving the surface is just equal to the number of molecules coming back to it at a constant temperature. The molecules which are in a liquid state at any moment may be in vapour state in the next moment

Factors on which vapour pressure does not depend

The magnitude of vapour pressure does not depend upon the:

(a) Amount of liquid

(b) Volume of container

(c) Surface area of liquid

The larger surface area also presents a larger target for returning molecules. So rate of condensation also increases

Factors on which vapour pressure depends

(i) Temperature

At an elevated temperature, the kinetic energy of molecules is enhanced and capability to leave the surface increases. It causes the increase of vapour pressure. Increases of vapour pressure goes on increasing for the same difference of temperature from 0°C to 100°C for water. There is increase of vapour pressure from 4.579 torr to 9.209 torr for change of temperature from 0°C to 10°C. But the increase is from 527.8 torr to 760 torr when temperature changes from 90°C to 100°C.

Vapour pressures of water (torr) at various temperatures

Temperature (°C)	Vapour Pressure (torr)
0	4.579
10	9.209
20	17.54
30	31.82
37	47.07
40	55.32
50	92.51
60	149.4
70	233.7
80	355.1
90	527.8
100	760.0

(ii) Strength of intermolecular forces

The difference in the strength of intermolecular forces in different liquids is directly related to their vapour pressures at a particular temperature. The stronger the intermolecular forces lower is the vapour pressure. At 20°C isopentane has the highest vapuor pressure while glycerol has lowest.

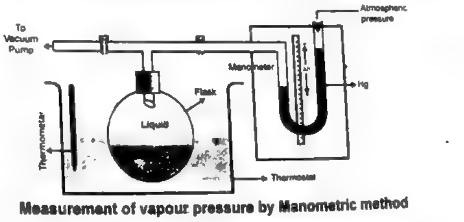
Name of compound	Vapour pressure at 20°C
Isopentane	580 torr
Ethyl ether	442.2 torr
Chloroform	170 torr
Carbon tetrachloride	87 torr
Water	43.9 torr
Mercury	0.012 torr
Glycerol	0.00016 torr

Measurement of Vapour Pressure

There are many methods for measurement of vapour pressure of a liquid. One of the most important methods is given below:

Manometric Method

It is comparatively an accurate method. The liquid whose vapour pressure is to be determined is taken in a flask placed in a thermostat. One end of the tube is connected to a manometer and the other end is connected to a vacuum pump. The liquid is frozen with the help of freezing mixture and the space above the liquid is evacuated. In this way, the air is removed from the surface of the liquid along with the vapours of that liquid. The frozen liquid is then melted to release any entrapped air. Liquid is again frozen and released air is evacuated. This process is repeated many times till almost all the air is removed.



Measurement of vapour pressure by Manometric method

Now the liquid is warmed in the thermostat to that temperature at which the vapour pressure of the liquid in the flask is to be determined. Difference in the heights of the columns of Hg in the two limbs of the manometer determines the vapour pressure of the liquid

The column of mercury in the manometer facing the vapours of the liquid is depressed. The other column, which faces the atmospheric pressure, rises. Actually, the pressure on the surface of the liquid in the flask is equal to the sum of the atmospheric pressure and vapour pressure of liquid. For this reason, the column of manometer facing the liquid is more depressed than facing the atmosphere and it is given by the following equation:

$P = P_a + \Delta h$

P = Vapour pressure of liquid at 1 atm pressure

P_a = Atmospheric pressure

Δh = Difference in the heights of the mercury levels in the two limbs of the manometer, giving us the vapour pressure of liquid.

Dynamic equilibrium is established during evaporation of a liquid in a closed vessel at constant temperature.

Ans. When the molecules of a liquid leave the open surface, they are mixed up with the air above the liquid. But if we close the system, the molecules of the liquid start gathering above the surface. They not only collide with the walls of container but also with the surface of liquid and may be recaptured by liquid surface. This process is called condensation. The two processes i.e., evaporation and condensation continue till the rate of evaporation becomes equal to the rate of condensation. It means that the number of molecules leaving the surface is equal to the number of molecules re-captured by the surface at constant temperature. This is the state of dynamic equilibrium.

Q10. Explain the term saturated vapour pressure. Arrange in order of increasing vapour pressure: 1 dm³ of water, 1 dm³ of ethanol, 50 cm³ of water, 50 cm³ of ethanol and 50 cm³ of ether.

Ans **Saturated Vapour Pressure**

"The process of evaporation in a closed container will proceed until there are as many molecules returning to the liquid as there are escaping. At this point the vapour is said to be saturated, and the pressure of that vapour is called the saturated vapour pressure."

- Vapour pressure doesn't depend upon the amount of liquid.
- Vapour pressure is inversely proportional to the intermolecular forces.

Between **ether molecules**, there are weak dipole-dipole forces and its vapour pressure is high.

Intermolecular forces in case of **ethanol** are hydrogen bonding, stronger than dipole-dipole force of ether. That's why its vapor pressure is lesser than ether.

Intermolecular forces in **water** are hydrogen bonding which are still stronger than ethanol.

Hence, its vapour pressure is the least.

The increasing order of vapor pressure for these liquids is as follows.

50 cm^3 of ether > 50 cm^3 of ethanol = 1 dm^3 of ethanol > 50 cm^3 of water = 1 dm^3 of water.

BOILING POINT

"The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure/external pressure is called boiling point."

Explanation

When a liquid is heated, the vapour pressure goes on increasing. A stage reaches when the vapour pressure of the liquid becomes equal to the external atmospheric pressure. This temperature is called the boiling point of the liquid. The reason for this is that the bubbles of vapours which are formed in the interior of the liquid have greater internal pressure than atmospheric pressure on the surface of liquid. This thing makes the bubbles to come out of the liquid and burst upon the surface. Thus a constant stream of bubbles comes out at the boiling point.

Boiling points of some common liquids at 760 torr

Liquids	B.P (°C)	Liquids	B.P(°C)
Acetic Acid	118.50	Carbon tetrachloride	76.50
Acetone	56.00	Ethanol	78.26
Aniline	184.4	Naphthalene	218.00
Benzene	80.15	Phenol	181.80
Carbon disulphide	46.30	Water	100.00

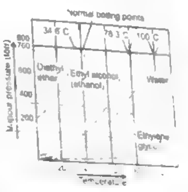
Molar Heat of Vapourization

"The amount of heat required to vapourize one mole of a liquid at its boiling point is called its molar heat of vapourization."

e.g. Molar heat of vapourization of water is 40.6 $kJmol^{-1}$.

Explanation

When a liquid is heated, the kinetic energy of its molecules increases and hence the temperature also increases. At the boiling point, the kinetic energy of the molecules becomes maximum and any further heating at this stage will not increase the temperature. This heat will only be utilized to break the intermolecular forces and convert the liquid into its vapours.



Temperature-Vapour Pressure Graph

This graph shows that the liquids reach up to their boiling points when their vapour pressures are equal to 760 torr at sea level. The way these curves start at 0°C is interesting. Water takes start at 4.8 torr while diethyl ether at around 200 torr. This is due to difference in the strengths of their intermolecular forces. The curve for water goes along with temperature axis to a greater extent at the beginning as compared to ether. It means that water can hardly overcome its intermolecular forces at low temperatures. It is clear from the curves that the vapour pressure increases very rapidly when the liquids are closer to their boiling points.

Boiling Point and External Pressure

Principle

The boiling point of a liquid is directly proportion to the external pressure.

- When the external pressure is high, the liquid requires greater amount of heat to equalize its vapour pressure to external pressure. In this way boiling point is raised.
- Similarly, at a lower external pressure, a liquid absorbs less amount of heat and it boils at a lower temperature.
- A liquid can be made to boil at any temperature by changing the external pressure.

External pressure (torr)	Boiling point (°C)
1489 torr	120°C
760 torr (at sea level)	100°C
700 torr (at Murree Hills)	98°C
323 torr (at Mount Everest)	69°C
23.7 torr	25°C

Boiling points of water at various external pressure

Applications of Boiling Point

Pressure Cooker

Principle

The working principle of pressure cooker is that:

"The boiling point of a liquid increases with increased external pressure."

Working

(i) Formation of vapours

When a liquid (say H_2O) is heated in a pressure cooker, which is a closed container, more and more vapours are formed over the surface of the liquid, exerting more pressure.

(ii) Increase in pressure

These vapours are not allowed to escape. In this way, they develop more pressure in the cooker and the boiling point of H_2O increases. As, more heat is absorbed in water. So, food is cooked quickly under increased pressure.

Vacuum Distillation

"The process of heating the liquid under reduced pressure to change it into vapours at a lower temperature and then condensing the vapours to a liquid is called vacuum distillation."

Principle

"The boiling point of a liquid can be decreased by decreasing the external pressure."

Working

Some liquids with high boiling points may decompose during distillation. In order to boil or distil them at lower temperature, pressure is lowered or distillation is carried out under vacuum (vacuum distillation).

Example

Glycerin boils at 290°C at 760 torr (1 atm) pressure but decomposes at this temperature. Hence, glycerin cannot be distilled at 290°C. Under vacuum, the boiling point of glycerin decreases to 210°C at 50 torr. It is distilled at the temperature without decomposition and hence can be purified easily.

Advantages

- It decreases the time for the distillation process.
- It is economical because less fuel is required.
- The decomposition of many substances can be avoided

(iii) Boiling needs a constant supply of heat:

Ans. When a liquid is heated, the kinetic energy of its molecules increases and hence the temperature also increases. At the boiling point, the kinetic energy of the molecules becomes maximum and any further heating at this stage will not increase the temperature. This heat will only be utilized to break the intermolecular forces and convert the liquid into vapours. A decrease in temperature at this stage reduces the rate of boiling.

(vii) The boiling point of water is different at Murree hills and at Mount Everest:

Ans. The boiling point of a liquid is directly proportional to its external pressure. As the external pressure increases, the boiling point also increases and vice versa. At 760 torr the boiling point of water is 100°C.

Boiling point of water at Murree: Since at Murree, the external pressure reduces to 700 torr so, the boiling point decreases to 98°C

Boiling point at Mount Everest: At Mount Everest, the external pressure is 323 torr so, the boiling point is also less i.e., 69°C.

(viii) Vacuum distillation can be used to avoid decomposition of a sensitive liquid:

Ans. **Vacuum distillation:** "The process of heating the liquid under reduced pressure to change it into vapours at a lower temperature and then condensing the vapours to a liquid, is called vacuum distillation."

Vacuum distillation has many advantages.

(i) It decreases the time for the distillation process.
(ii) It is economical because less fuel is required.
(iii) The decomposition of many compounds can be avoided

Example: Glycerin boils at 290°C at 760 torr pressure but decomposes at this temperature. Hence, glycerin cannot be distilled at 290°C. Under vacuum, the boiling temperature of glycerin decreases to 210°C at 50 torr. It is distilled at this temperature without decomposition and hence can be purified easily.

Energetics of Phase Changes

Whenever, matter undergoes a physical change, it is always accompanied by an enegy change. This change in energy is mostly in the form of heat and is the quantitative measurement of the difference in the strength of intermolecular forces

Enthalpy Change (ΔH)

"If a physical or a chemical change takes place at a constant pressure, then the heat change during this process is called enthalpy change"

Type of Enthalpy Changes

(i) Molar Heat of Fusion (ΔH_f)

"It is the amount of heat absorbed by one mole of a solid when it melts into liquid form at its melting point." The pressure, during the change is kept one atmosphere

Molar Heat of Vapourization (ΔH_v)

"It is the amount of heat absorbed when one mole of a liquid is changed into vapours at its boiling point." The pressure, during the change is kept one atmosphere.

Molar Heat of Sublimation (ΔH_s)

"It is the amount of heat absorbed when one mole of a solid sublimes to give one mole of vapours at a particular temperature and one atmospheric pressure"

Note: All these enthalpy changes are positive, because they are endothermic processes.

Prove that $\Delta H_s >> \Delta H_v > \Delta H_f$

When a solid substance melts then atoms, molecules or ions undergo relatively small changes in intermolecular distances and the potential energy also undergoes a small change. But when a liquid evaporates, then larger changes in intermolecular distances and in potential energy takes place. So ΔH of vapourization of a substance is greater than ΔH of fusion. The values of ΔH_s are even larger than ΔH_v because attractive forces in solids are stronger than those in liquids. So we can say

$$\Delta H_s >> \Delta H_v > \Delta H_f$$

The values of ΔH_v and ΔH_s tell us directly the energy needed two separate molecules from each other. So from these values, we can compare the strengths of intermolecular forces in different compounds.

Causes of ΔH_v

ΔH_v for H_2O, NH_3 and SO_2 are reasonably high due to polar nature of molecules. ΔH_v for iodine is the highest amongst its family members due to its greater polarizability. Similarly, hexane (C_6H_{14}) has the highest ΔH_v value amongst the given hydrocarbons due to larger size of its molecules. Actually, the London dispersion forces in I_2 and C_6H_{14} are sufficiently strong and these are responsible for such a behavior.

Heat of vaporization of some substances

Substance	ΔH_v (kJ/mol)
H_2O	+40.6
NH_3	+21.7
HCl	+15.6
SO_2	+24.3
F_2	+5.9
Cl_2	+10.00
Br_2	+15.00
I_2	+22.00
CH_4	+8.60
C_2H_6	+15.1
C_3H_8	+16.9
C_6H_{14}	+30.1

Change of State and Dynamic Equilibrium

Whenever, a change of state occurs, the system moves towards the condition of dynamic equilibrium. Dynamic equilibrium is a situation when two opposing changes occur at equal rates. The dynamic equilibrium is the fate or the ultimate goal of all the reversible chemical reactions and all the physical changes.

$$\text{Ice} \rightleftharpoons \text{water}$$

(ix) Heat of sublimation of a substance is greater than that of heat of vaporization:

Ans. **Molar heat of vaporization:** "The amount of heat absorbed when one mole of a liquid is changed into vapours at its boiling point, is called heat of vaporization." The pressure during the change is kept one atmosphere.

When a liquid is converted into vapours, then atoms, molecules or ions undergo small change in **inter-molecular distances and potential energy.**

Molar heat of sublimation: "The amount of heat absorbed when one mole of a solid sublimes to give one mole of vapours at a particular temperature and one atmospheric pressure."

When a solid is directly converted into vapours, then it undergoes large change in **intermolecular distances and potential energy.**

Hence:

$$\Delta H_s > \Delta H_v$$

Example: Molar heat of vaporization of water = 40.67 kJ mol^{-1}.
Molar heat of sublimation of water = 46.7 kJ mol^{-1}.

Heat of sublimation of iodine is very high:

Ans. **Heat of Sublimation:** "The amount of heat absorbed when one mole a solid sublimes to form vapours at a particular temperature and one atmospheric pressure."

Iodine (I_2) is a non-polar molecule. Due to its larger size, it has high polarizability. Hence, **London dispersion** forces are sufficiently stronger in iodine (I_2). As a result, a large amount of energy is required to sublime iodine.

Q. 13 What are liquid crystals? Give their uses in daily life.

Liquid Crystals

"The turbid liquid phase of a solid that exists in between the melting and clearing temperature is called liquid crystal."

$$\text{Crystal} \rightleftharpoons \text{Liquid Crystal} \rightleftharpoons \text{Liquid}$$

Discovery

In 1888, Frederick Reinitzer, an Austrian botanist discovered the liquid crystals. He was studying an organic compound cholesteryl benzoate. This compound turns milky liquid at 145°C and becomes a clear liquid at 179°C. When the substance is cooled, the reverse process occurs. This turbid liquid phase was called liquid crystal.

Characteristics

Liquid crystals has both properties of liquids and crystals (solid).

Liquids like properties: Viscosity, surface tension, fluidity etc.

Crystals like properties: Optical properties, molecules have some orderly arrangement.

In short we can say that the properties of liquid crystals are intermediate between those of crystals and isotropic liquids.

Isotropic nature

A crystalline solid may be isotropic or anisotropic but liquid crystals are always anisotropic.

Types

Those substances which make the liquid crystals are often composed of long rod like molecules. In the normal liquid phase, these molecules are oriented in random directions. In liquid crystalline phase, they develop some ordering of molecules. Depending upon the nature of ordering, liquid crystals can be divided into

(i) Nematic (ii) Smectic (iii) Cholesteric

Uses of Liquid Crystals

(i) As temperature sensor

Like solid crystals, liquid crystals can diffract light. When one of the wavelengths of white light is reflected from a liquid crystal, it appears coloured. As the temperature changes, the distances between the layers of the molecules of liquid crystals change. Therefore, the reflected light changes accordingly. Thus liquid crystals can be used as temperature sensors.

(ii) To find potential failure/as room thermometers

Liquid crystals are used to find the point of potential failure in electrical circuits. Room thermometers also contain liquid crystals with a suitable temperature range. As the temperature changes, figures show up in different colours.

(iii) Medical diagnosis

Liquid crystals are used to locate the veins, arteries, infections and tumors. The reason is that these parts of the body are warmer than the surrounding tissues. Specialists can use the techniques of skin thermography to detect blockages in veins and arteries. When a layer of liquid crystal is painted on the surface of the breast, a tumor shows up as a hot area which is coloured blue. This technique has been successful in the early diagnosis of breast cancer.

(iv) Electrical devices

Liquid crystals are used in the display of electrical devices such as digital watches, calculators and laptop computers. These devices operate due to fact that temperature, pressure and electromagnetic fields easily affect the weak bonds which hold molecules together in liquid crystals.

(v) Solvents in chromatography

In chromatographic separations, liquid crystals are used as solvents.

(vi) Oscillograph and TV displays

Oscillograph and TV displays also use liquid crystal screens.

KEY POINTS

1) Among three states of matter i.e. gases, liquids and solids, the intermolecular attractive forces in the gases are negligible. In liquids intermolecular forces are strong enough to keep the molecules close together. Anyhow, the molecules in liquids are free to move with respect to one another. In solids the particles occupy specific locations in three dimensional arrangements. Molecules in liquids are free to move with respect to one another. In solids the particles occupy specific locations in three dimensional arrangement.

2) There are four types of intermolecular forces i.e. dipole-dipole forces, London dispersion forces, hydrogen bonding and Ion-dipole forces. The relative strengths of dipole-dipole and dispersion forces depend upon the polarity, polarisability, size and shape of the molecules. Hydrogen bonding occurs in compounds containing O-H, N-H, H-F bonds.

3) The vapour pressure of a liquid measures the tendency of a liquid to evaporate. It is the pressure exerted by the vapours on the surface of a liquid when the rate of evaporation is equal to the rate of condensation. A liquid boils when its vapour pressure equals the external pressure.

4) Many crystalline solids melt to give a turbid liquid before melting to give a clear liquid. These turbid liquids possess some degree of order and are called liquid crystals. Liquid crystals have the fluidity of liquids and the optical properties of solids.

SOLVED OBJECTIVE EXERCISE

Q1. Choose the best answer from the given choices.

(i) London dispersion forces are the only forces present among the:
- (a) molecules of water in liquid state
- (b) atoms of helium in gaseous state at high temperature
- (c) molecules of solid iodine
- (d) molecules of hydrogen chloride gas

(ii) Acetone and chloroform are soluble in each other due to:
- (a) Intermolecular hydrogen bonding
- (b) ion-dipole interaction
- (c) instantaneous dipole
- (d) all of the above

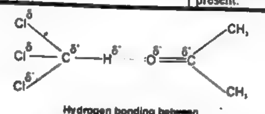
(iii) NH_3 shows a maximum boiling point among the hydrides of Vth–A group elements due to
- (a) very small size of nitrogen
- (b) lone pair of electrons present on nitrogen
- (c) enhanced electronegative character of nitrogen
- (d) pyramidal structure of NH_3

(iv) When water freezes at 0°C, its density decreases due to:
- (a) cubic structure of ice
- (b) empty spaces present in structure of ice
- (c) instantaneous dipole
- (d) change of bond angles

(v) In order to mention the boiling point of water at 110°C, the external pressure should be:
- (a) between 760 torr and 1200 torr
- (b) between 200 torr and 760 torr
- (c) 765 torr
- (d) any value of pressure

Solved Exercise MCQ's

Q. No	Answer	Reason		
(i)	(c) molecules of solid iodine		Substance	Intermolecular Forces
		(a)	molecules of water in liquid state	In H_2O, H-Bonding Dipole dipole forces and London forces are

				present.
		(b)	atoms of helium in gaseous state at high temperature	No attractive force.
		(c)	molecules of solid iodine	I_2, being non polar, have only London forces.
		(d)	molecules of hydrogen chloride gas	HCl is a polar molecule. So DDF and London forces are present.
(ii)	**(a) Intermolecular hydrogen bonding**	 Hydrogen bonding between chloroform and acetone		
(iii)	**(c) enhanced electronegative character of nitrogen**	Enhanced electronegative character of nitrogen makes it suitable for hydrogen bonding. It has high boiling point (–33.4 °C) than other hydrides of its group except SbH_3 (B.P = –17°C)		
(iv)	**(b) empty spaces present in structure of ice**	Due to hydrogen bonding empty spaces create in the structure of ice. That is why greater volume decreases the density of ice.		
(v)	**(a) between 760 torr and 1200 torr**	• Boiling point of water at 760 torr = 100°C • Boiling point of water at 1489 torr = 120°C So boiling point of water at 110 °C requires external pressure between 760 torr and 1200 torr.		

Q2. Fill in the blanks with suitable words.

(i) The polarizability of noble gases ________ down the group and results in the increase in their boiling points.
(ii) ________ is developed in acetone and chloroform when they are mixed together.
(iii) Exceptionally weak ________ of HF is due to strong hydrogen bonding present in it.
(iv) The concept of dynamic equilibrium is the ultimate ________ of all reversible reactions.
(v) ΔH_v of C_6H_{14} should be ________ than that of C_2H_6.
(vi) During the formation of ice from liquid water there is a ________% increase in volume.
(vii) The rate of increase of vapour pressure of water ________ at high temperatures.
(viii) A layer of ice on the surface of water ________ the water underneath for further heat loss.
(ix) Evaporation is a ________ process.
(x) Liquid crystals are used in the display of ________ devices.

ANSWERS

(i) increases	(ii) hydrogen bonding
(iii) acidic strength	(iv) goal
(v) greater	(vi) 9
(vii) increases	(viii) insulates
(ix) cooling	(x) electrical

Q3. Indicate 'true' or 'false' as the case maybe.

(i) Dipole-dipole forces are weaker than dipole-induced dipole forces.
(ii) The ion dipole interactions are responsible for the dissolution of an ionic substance in water.
(iii) The high polarizability of iodine is responsible for its existence in solid form and its difference from other halogens.
(iv) The strong hydrogen bonding in H_2S makes it different from water.
(v) Hydrocarbons are soluble in water because they are polar compounds.
(vi) The viscosities of liquids partially depend upon the extent of hydrogen bonding.
(vii) The state of equilibrium between liquid state and vapours is dynamic in nature.
(viii) Heat of vapourization of liquids depend upon the intermolecular forces of attraction present between their molecules.
(ix) Ice does not show any vapour pressure on its surface at –1°C.
(x) Boiling point of a liquid is independent of external pressure.

ANSWERS

(i) False	(ii) True	(iii) True	(iv) False	(v) False
(vi) True	(vii) True	(viii) True	(ix) False	(x) False

SHORT ANSWERS TO EXERCISE

LIQUIDS

Q.6 (b) All gases have a characteristic critical temperature. Above the critical temperature it is impossible to liquefy a gas. The critical temperatures of carbon dioxide and methane are 31.14°C and -81.9°C respectively. Which gas has the stronger intermolecular forces? Briefly explain your choice?

Ans. CO_2 is a linear molecule whereas CH_4 is a tetrahedral molecule. Intermolecular forces in CO_2 are stronger than CH_4 although both molecules are non-polar in nature. Both have instantaneous dipole-induced dipole forces. Critical temperature of gas depends upon the intermolecular forces, shape and size of molecules. Critical temperature of CO_2 is higher than CH_4 which show that intermolecular forces in CO_2 are stronger than in CH_4. In both cases, intermolecular forces are instantaneous dipole induced dipole forces.

Q.7 Three liquids have the properties mentioned against their names

		Water	Propanone	Pentane
(i)	Molecular formula	H_2O	C_3H_6O	C_5H_{12}
(ii)	Relative molecular mass (amu)	18	58	72
(iii)	Enthalpy change of vapourization $kJ\,mol^{-1}$	41.1	31.9	27.7
(iv)	Boiling point (°C)	100	56	36

(a) What type of intermolecular force predominates in each liquid?
(i) water (ii) Propanone (iii) Pentane

Ans. (i) In water, hydrogen bonding is present.
(ii) In propanone C_3H_6O, dipole-dipole forces are present.
(iii) In pentane (C_5H_{12}), instantaneous dipole-induced dipole forces or London dispersion forces are present.

(b) What do you deduce about the relative strength of these forces in the liquids? Justify your conclusions.

Ans. Relative strength of intermolecular forces in water, propane and pentane is

Water > Propane > Pentane

Reason: Boiling point of the given compounds show the relative strength of the intermolecular forces. Boiling point of the liquid depends upon the strength of intermolecular forces. The boiling point of water is higher than propane which is higher than pentane which show that intermolecular forces is the following order

Water > Propane > Pentane

(c) If the liquids are shaken together in pairs,

(i) Which pair would be unlikely to mix?

Ans. Water and Pentane

(ii) Explain this immiscibility in terms of the forces between the molecules.

Ans. Water is a polar whereas pentane is non-polar we Know that "Like dissolves like" So both liquids are invincible

(iii) Choose one of the pairs that mix and say whether the enthalpy change on mixing would be positive or negetive.

Ans. Pentane is miscible with propanone.

Reason: Both are non-polar molecule and due to London forces, they are soluble in each other This process of mixing is an exothermic and heat is evolved therefore enthalpy change will be negative.

Q. 8 Describe the various forces responsible for keeping the particles together in the following elements and compounds and their effects on physical properties making use of the data below.

Substance	Formula	Molar Mass (amu)	M.P (°C)
Neon	Ne	20	-248
Argon	Ar	40	-189
Water	H_2O	18	0
Sodium fluoride	NaF	42	993
Diamond	C	12	3350

Ans. **Neon:** London-dispersion forces are present in neon. These are weak intermolecular forces, therefore neon has low boiling point and low heat of vaporization.

Argon: London-dispersion forces are present in argon. Argon has low boiling point and low heat of vaporization But these properties have greater value than neon because size of argon is greater than neon

Water: In water, molecular hydrogen bonding is present. The boiling point and heat of vaporization of water is high due to hydrogen bonding.

Sodium Fluoride (NaF): Ionic bond is present between positive and negative ions. These electrostatic forces of attraction are very strong Due to this, sodium fluoride has high boiling point and high lattice energy

Diamond: In case of diamond carbon atoms have network of covalent bonds. It is very hard It has very high boiling point It is insoluble in polar solvent. It is bad conductor of electricity

Q. 9 The boiling points and molar masses of hydrides of some first row elements are tabulated below:

Substance	Boiling Point (K)	Molar Mass (g mol⁻¹)
CH_4	109	16
NH_3	240	17
H_2O	373	18

Q. Suggest reasons for the difference in their boiling points in terms of the type of molecules involved and the nature of the forces present between them.

Ans. CH_4 : Methane is a non-polar molecule. It has London dispersion forces. These forces are very weak so it has low bonding point

NH_3 : Ammonia is a polar molecule. It has hydrogen bonding between its molecules These intermolecular forces are stronger than London forces. Due to these forces, ammonia has high boiling point and heat of vaporization than methane

H_2O : Water is a polar molecule. In water molecule strong hydrogen bonding is present. The affect of hydrogen bonding in water is more than in ammonia. Due to this, boiling point and heat of vaporization of water is very high as compare to methane and ammonia.

Q. 11 While a volatile liquid standing in a breaker evaporates, the temperature of the liquid remains the same as that of its surrounding. If the same liquid is allowed to vaporurise into atmosphere in an insulated vessel, its temperature falls below that of its surrounding. Explain the difference in behavior.

Ans. Beaker is an open container. Heat exchanges between liquid (system) and its surrounding. So when liquid evaporates, it temperature decreases and heat flows from surrounding to the liquid In this way the temperature of the liquid and its surrounding remains the same. On the other hand, in an insulated vessel, no heat exchange takes place between liquid and its surrounding. So during evaporation, temperature of liquid decreases. Since no heat moves from surrounding to liquid, so its temperature falls below that of its surrounding.

Additional Questions

Q. Define Polarizability:

Ans. "The quantitative measurement of the extent to which the electronic cloud can be polarized or distorted is called polarizability "

As the size of the molecules increases the distortion also increases. This increased distortion of electronic cloud creates stronger London dispersion forces and hence the values of thermodynamic parameters increases

Q. Why does ice float on water?

Ans. When the temperature of water is decreased and ice is formed then molecules become more regular and this regularity extends throughout the whole structure. Empty spaces are created in the structure That is why when water freezes it occupies 9% more space and its density decreases. The result is that ice floats on water

PREVIOUS BOARD QUESTIONS

Q. Ethane is a gas while hexane is a liquid. Give reason.

Q. Why the boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes?

Q. Why fish and plants continue to survive under frozen water?

Q. Liquid boils at constant temperature at a given pressure. Why?

Q. How liquid crystals can act as temperature sensors?

Q. How the rate of evaporation depends on the surface area but vapour pressure does not depend upon surface area?

Q. Steam causes more severe burns than does the boiling water Give reason

Q. Polar compounds are soluble in polar solvents. Justify the statement

Q. Give significance of lower density of ice than water.

Q. Why the vapor pressures of water ethyl alcohol and diethyl ether are different from each other at 0°C?

Q. A liquid boils at that temperature when its vapor pressure becomes equal to the external pressure. Why?

SOLIDS

"Those substances which are rigid, hard, having definite shape and definite volume and cannot flow are called solids."

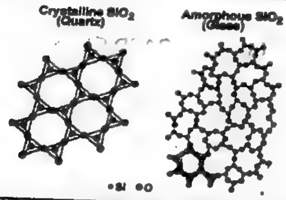
Important points

- The atoms, ions or molecules that make up a solid are closely packed.
- They are held together by strong cohesive forces.
- The constituent particles of solids cannot move at random. They show only vibrational motion.
- There exists a well ordered arrangement in solids,

Difference between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and chracteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they into two pieces and the newly generated surfaces are plain and smooth.	When cut with a sharp edged tool , they cut into two pieces with irregular surfaces.
Heat of fusion	They have a definite and characteristic heat of fusion.	They do not have definite heat of fusion.
Anisotropy	Anisotropic in nature	Isotropic in nature.
Nature	True solids	Pseudo solids or super cooled liquids or highly viscous liquids.
Order in arrangement of constituent particles	Long range order	Only short range order
Examples	NaCl, Sugar, Ice, Diamond etc.	Rubber, Plastic, Glue, Glass, Paper etc.

Crystalline SiO_2 (Quartz) Amorphous SiO_2 (Glass)



•Si •O

(vi) Amorphous solid like glass is also called super cooled liquid.

Ans. Amorphous substances are those whose constituent atoms, ions or molecules do not possess regular orderly arrangement. Many crystalline solids can be changes into amorphous solids by melting them and then cooling the molten mass rapidly. In this way the constituent particles do not find time to arrange themselves, These substances have solid state properties and virtually complete maintenance of shape and volume. But they are in fact liquids cooled below their freezing point without crystallization. Therefore, amorphous solid like glass is also called super cooled liquid.

Q. How can you convert crystalline solid into amorphous solid

Many crystalline solids can be changed into amorphous solids by melting them and then cooling the molten mass rapidly. In this way, the constituent particles do not find time to arrange themselves Thus a crystalline solid is changed into amorphous solid.

Q. What are crystallites?

- "The small part of amorphous solids which possess orderly arrangements of constituent particles are called crystallites."

PROPERTIES OF CRYSTALLINE SOLIDS

(1) Geometrical Shape

All the crystalline solids have a definite distinctive geometrical shape due to definite and orderly arrangement of atoms, ions or molecules in three dimensional space. For a given crystal, the interfacial angles, at which the surfaces intersect are always the same no matter in which shape, they are grown. The faces and angles remain characteristic even when the material is ground to a fine powder.

(2) Melting Points

Crystalline solids have sharp melting points and can be identified from their definite melting points

(3) Cleavage Planes

Whenever the crystalline solids are broken they do so along definite planes. These planes are called the cleavage planes. They are inclined to one another at a particular angle for a given crystalline solid. The value of this angle varies from one solid to another solid.

(4) Anisotropy

"The phenomenon in which a crystalline solid shows variation in certain physical properties depending upon the direction is called anisotropy."

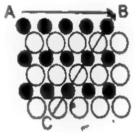
Anisotropic properties:

Anisotropic properties are:

- Refractive index.
- Thermal and electrical conductivities.
- Co-efficient of thermal expansion.
- Cleavage planes.

Reason

The variation in anisotropic properties with direction is due to the fact that the orderly arrangement of particles in crystalline solids is different in different directions.



In figure,

From A – B = same kind of particles in this direction

C – B = different kind of particles in this direction

Examples

(i) Electrical conductivity of graphite is greater in one direction than in another. Actually, electrons in graphite are mobile for electrical conduction parallel to the layers only. Therefore, its conductivity in this direction is far better than perpendicular to the other direction.

(ii) Cleavage itself is an isotropic behaviour.

(vii) Cleavage of the crystals is itself anisotropic behaviour.

Ans. In crystals, the particles are arranged in a regular repeating three dimensional pattern. This arrangement of particles is different in different planes. It is due to the reason that cleavage of crystals occur differently in different directions. Hence, cleavage of crystals is itself anisotrópic behaviour. Difference in physical properties with direction.

(5) Symmetry

"The repetition of angles, edges or faces when a crystal is rotated about 360° along its axis is called symmetry."

Symmetry elements

Following are the symmetry elements of a crystal:

(i) Plane of symmetry
(ii) Axis of symmetry
(iii) Centre of symmetry.

(6) Habit of a Crystal

"The shape of a crystal in which it usually grows is called habit of a crystal."

Preparation

A crystal can be prepared:

(i) By moderate cooling of a saturated solution.
(ii) By slow cooling of a liquid

These are formed by growing in various directions

Change in habit of a crystal

If the conditions for growing a crystal are maintained, then the shape of the crystal always remains the same. If the conditions are changed, the shape of the crystal may change.

For example, a cubic crystal of NaCl becomes needle like when 10% urea is present in its solution as an impurity.

(7) Isomorphism

"The phenomenon in which two different substances exist in the same crystalline form is called isomorphism."

Isomorphs

"Those crystalline substances which have same crystalline form are isomorphs to each other."

- Isomorphs may be compounds or elements.

Examples

Isomorphs	Crystalline Form	Atomic Ratio
$NaNO_3$, KNO_3	Rhombohedral	1 : 1 : 3
K_2SO_4, K_2CrO_4	Orthorhombic	2 : 1 : 4
$ZnSO_4$, $NiSO_4$	Orthorhombic	1 : 1 : 4
NaF, MgO	Cubic	1 : 1
Cu, Ag	Cubic	1 : 1
Zn, Cd	Hexagonal	1 : 1

Similarities and dissimilarities of isomorphs

Similarities	Dissimilarities
Same crystalline form	Different physical properties
Same atomic ratio	Different chemical properties
Same way of combination	Different nature of atoms
Same number of atoms	
Same structure of anions	

- The structures of the negatively charged ions like NO_3^{1-} and CO_3^{2-} are the same and they have triangular planar structure.
- Both SO_4^{2-} and CrO_4^{2-} have tetrahedral structure.

(viii) The crystals showing isomorphism mostly have same atomic ratios.

Ans. The crystals which show isomorphism have same crystalline form and depends upon the number of atoms and their way of combination. Isomorphic substances have equal number of atoms linked with each other in similar ways. Different crystals can show isomorphism only when they have same atomic ratios. e.g. $NaNO_3$ and KNO_3 are isomorphs. They have rhombohedral crystalline form and they have same atomic ratio that is 1:1:3

(8) Polymorphism

"The phenomenon in which a compound exists in more than one crystalline forms is called polymorphism."

Polymorphs

"The compound which exists in more than one crystalline forms is called polymorphic compound and these forms are polymorphs of each other."

Examples

Substance	Crystalline Forms
$AgNO_3$	Rhombohedral and orthorhombic
$CaCO_3$	Trigonal and orthorhombic

Important points

- It is a compound phenomenon.
- Polymorphs have same chemical properties.
- Polymorphs have different physical properties due to the different structural arrangement of their particles.

(9) Allotropy

"The phenomenon in which an element exists in more than one crystalline forms is called allotropy and these forms of the element are called allotropes or allotropic forms."

Examples

Element	Allotropic Forms
Sulphur, S	Rhombic, monoclinic
Carbon, C	Cubic (diamond), hexagonal (graphite)
Tin, Sn	Grey tin (cubic), white tin (tetragonal)

Important points

- It is an elemental phenomenon.
- Allotropes of an element have same chemical but different physical properties.

Qs. (b) How "Polymorphism and Allotropy" are related to each other.

Polymorphism	Allotropy
"The phenomenon in which a compound exist in more than one crystalline form, is called polymorphism."	"The phenomenon in which an element exists in more than one crystalline form, is called allotropy."
◆ It is a compound phenomenon. ◆ They have same chemical	◆ It is an elemental phenomenon. ◆ They have same chemical

Polymorphism	Allotropy
properties but different physical properties.	properties but different physical properties.
Examples:	**Example:**
• $AgNO_3$ (Rhombohedral, orthorhombic)	• Sulphur (Rhombic, Monoclinic)
• $CaCO_3$ (Trigonal, orthorhombic)	• Carbon (Diamond, Graphite)
	• Tin (Grey tin [cubic], white tin [tetragonal])

(10) Transition Temperature

"The temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other is called transition temperature."

Examples

(i) Grey tin (cubic) $\xrightleftharpoons{13.2^\circ C}$ White tin (tetragonal)

(ii) Sulphur S_8 (rhombic) $\xrightleftharpoons{95.5^\circ C}$ Sulphur S_8 (monoclinic)

(iii) KNO_3 (orthorhombic) $\xrightleftharpoons{128^\circ C}$ KNO_3 (rhombohedral)

(iv) $Na_2SO_4.10H_2O \xrightleftharpoons{32.38^\circ C} Na_2SO_4 + 10H_2O$
(Hydrated form) (Anhydrous form)

(v) $Na_2CO_3.10H_2O \xrightleftharpoons{32.02^\circ C} Na_2CO_3.7H_2O + 3H_2O$
(Higher hydrated form) (Lower hydrated form)

Important points

- At transition temperature, one crystalline form of a substance changes to another.
- Above and below this temperature, only one form exists.
- The transition temperature of allotropic forms of an element is always less than its melting point.

(ix) The transition temperature is shown by elements having allotropic forms and by compounds showing polymorphism.

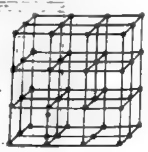
Ans. The elements which show allotropy have different crystalline forms, similarly the compounds which shows polymorphism have different crystalline forms. Each crystalline form is stable over a particular range of temperature. On heating, one crystalline form can be changed into another. The temperature at which one crystalline form changes into another is called transition temperature. Those substances which exist in single crystalline form do not have transition temperature. Hence, transition temperature is shown by elements and compounds having allotropic or polymorphic forms.

e.g. Sulphur S_8 (rhombic) $\xrightleftharpoons{95.5^\circ C}$ Sulphur S_8 (monoclinic)

KNO_3 (orthorhombic) $\xrightleftharpoons{128^\circ C}$ KNO_3 (rhombohedral)

CRYSTAL LATTICE

"An array of points representing atoms, ions or molecules of a crystal, arranged at different sites in three-dimensional space is called crystal lattice."



Lattice sites

"The points or sites representing atoms ions or molecules in a crystal lattice are called lattice point, or lattice sites."

The line joining the two points represents attraction between particles.

Q6. (a) Define unit cell. What are unit cell dimensions? How the idea of crystal lattice is developed from the concept of unit cell?

UNIT CELL

"The smallest part of the crystal lattice that has all the characteristic features of the entire crystal is called unit cell."

Important points

- A unit cell shows the structural properties of a given crystal.
- When a unit cell is repeated in three-dimensions, it gives the entire crystal.
- The complete information about a crystalline structure is present within its unit cell.

Unit cell dimensions/crystallographic elements

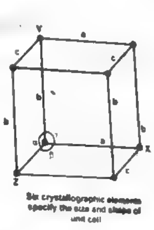
There are six (6) unit cell dimensions:

(A) Unit cell lengths

Length along x-axis = 'a'
Length along y-axis = 'b'
Length along z-axis = 'c'

(B) Unit cell angles

Angle between lengths 'a' and 'b' = γ
Angle between lengths 'b' and 'c' = α
Angle between lengths 'c' and 'a' = β



Six crystallographic elements specify the size and shape of unit cell

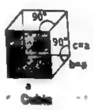
The unit cell lengths a, b, c may be assigned along x, y and z axis, respectively but angles α, β and γ have to be decided accordingly.

CRYSTALS AND THEIR CLASSIFICATION

Crystal System

"A crystal system may be identified by the dimensions of its unit cell along its three edges or axes a, b, c and three angles between the axes, α, β, γ."

There are seven crystal systems. These seven crystals systems are described as follow:



Cubic

1. Cubic System

Lengths

In this system, all the three axes are of equal lengths

$$a = b = c$$

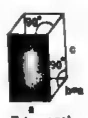
Angles

All axes are at right angles to each other.

$$\alpha = \beta = \gamma = 90^\circ$$

Examples

Fe, Cr, Ag, Au, NaCl, NaBr, Diamond etc.



Tetragonal

2. Tetragonal System

Lengths

In this system two axes are of equal lengths and the third axis is either shorter or larger than the other two.

$$a = b \neq c$$

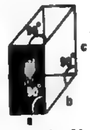
Angles

All the angles are of 90°

$$\alpha = \beta = \gamma = 90^\circ$$

Examples

Sn, SnO_2, MnO_2, NH_4Br etc.



Orthorhombic

3. Orthorhombic or Rhombic System

Lengths

All the three axes are of unequal length

$$a \neq b \neq c$$

Angles

All axes are at a right angle to each other.

$$\alpha = \beta = \gamma = 90^\circ$$

Examples

Iodine, Rhombic sulphur, $BaSO_4$, K_2SO_4 etc.

4. Rhombohedral or Trigonal System

Rhombohedral

Lengths

All the three axes are of equal length:

$$a = b = c$$

Angles

The three angles are not equal and lie between 90° and 120°.

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

Examples

Bi, Al_2O_3, $NaNO_3$, KNO_3 etc.

5. Hexagonal System

Hexagonal

Lengths

In this system, two axes are of equal length and the third axis is of different length.

$$a = b \neq c$$

Angles

Two axes are in one plane making an angle of 120° with each other and the third axis is at right angle to these two axes.

$$\alpha = \beta = 90^\circ, \gamma = 120^\circ$$

Examples

Graphite, ZnO, CdS, Ice, Zn, Cd etc.

6. Monoclinic System

Monoclinic

Lengths

In this system, all the three axes are of unequal length.

$$a \neq b \neq c$$

Angles

Two axes are at right angle to each other while the third angle is greater than 90°.

$$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$$

Examples

Sugar, sulphur, borax, $Na_2SO_4 . 10H_2O$ etc.

7. Triclinic system

Triclinic

Lengths

All the three axes are of unequal length.

$$a \neq b \neq c$$

Angles

All the three angles are unequal and none of these angles is 90°.

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

Examples

H_3BO_3, $K_2Cr_2O_7$, $CuSO_4.5H_2O$ etc.

Q.12 One of the unit cell angles of hexagonal crystal is 120°.

Ans. Hexagonal crystal is a regular polygon. The interior angles of a regular polygon of 'n' sides are always equal. The angle between regular sides of regular figure of 'n' sides

$= 180\left[\frac{n-2}{n}\right]$ degrees. Regular hexagon has 6 sides and angles in same plane

Hexagonal

$$n = 6$$

$$\text{angle} = 180\left[\frac{6-2}{6}\right]\text{degrees}$$

$$= 180\left[\frac{4}{6}\right]\text{degrees}$$

$$= 120^\circ$$

Sr. No.	Crystal System	Axes	Angles	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Fe, Cu, Ag, Au, NaCl, NaBr, diamond
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Sn, SnO_2, MnO_2, NH_4Br
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Iodine, Rhombic sulphur, $BaSO_4$, K_2SO_4
4.	Rhombohedral	$a = b = c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Bi, Al_2O_3, $NaNO_3$, KNO_3
5.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO, CdS, Ice, Zn, Cd
6.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Sugar, Monoclinic sulphur, Borax, $Na_2SO_4 . 10H_2O$
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	H_3BO_3, $K_2Cr_2O_7$, $CuSO_4 . 5H_2O$

CLASSIFICATION OF SOLIDS

There are four types of crystalline solids depending upon type of bonds present in them.

1. Ionic solids
2. Covalent solids
3. Molecular solids
4. Metallic solids

Q.7 (a) What are ionic solids? Give their properties.

Ionic Solids

Each ion is surrounded by oppositely-charged ions, forming a giant ionic lattice.

"The crystalline solids in which the particles forming the crystal are positively and negatively charged ions which are held together by strong electrostatic forces of attraction (ionic bond) are called ionic solids."

Examples

The crystals of NaCl, KBr etc. are ionic solids.

Properties of ionic solids

(i) Physical state

The cations and anions are arranged in a well defined geometrical pattern, so they are crystalline solids at room temperature. Under ordinary conditions of temperature and pressure they never exist in the form of liquids or gases.

(ii) Hardness, volatility, melting and boiling points

Ionic crystals are very stable compounds. Very high energy is required to separate the cations and anions from each other against the forces of attraction. That's why ionic solids are very hard, have low volatility and high melting and boiling points.

(iii) Nature of ionic solids

Ionic solids do not exist as individual neutral independent molecules. Their cations and anions attract each other and these forces are non-directional. The close packing of the ions enables them to occupy minimum space. A crystal lattice is developed when the ions arrange themselves systematically in an alternate manner.

(iv) Radius ratio

The structure of ionic crystals depends upon the radius ratio of cations and anions.

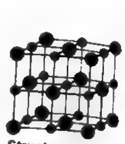
- **Radius ratio** $= \frac{r_+}{r_-}$

In NaCl

$$Na^+ = 95\text{ pm}$$
$$Cl^- = 181\text{ pm}$$
$$\text{Radius ratio} = \frac{95}{181} = 0.525$$

NaCl and CsF have the same geometry because the radius ratio in both the cases is the same.

(iii) Sodium chloride and cesium chloride have different structures.



Structure of NaCl

Ans. The structure of ionic crystals depends upon the radius ratio of cations and anions. If two ionic crystals have same radius ratio of cations and anions, then their structure will be same. The radius ratio of cations and anions in sodium chloride and cesium chloride is different. Hence they have different structure.

The radius of sodium ion $= r_+ = 0.95\,\mathring{A}$ The radius of chloride ion $= r_- = 1.81\,\mathring{A}$

$$\text{Radius ratio of NaCl} = \frac{r_+}{r_-} = \frac{0.95\,\mathring{A}}{1.81\,\mathring{A}} = 0.525$$

The radius of cesium ion $= r_+ = 1.69\,\mathring{A}$

$$\text{Radius ratio of CsCl} = \frac{r_+}{r_-} = \frac{1.69\,\mathring{A}}{1.81\,\mathring{A}} = 0.933$$

Structure of CsCl

This show that sodium chloride and cesium chloride have different radius ratios, so they have different structure.

(v) Formula mass of ionic solids

In the case of ionic crystals, we always talk about the formula mass of these substances and not the molecular mass because they do not exist in the form of molecules.

Q.12 (xiii) Ionic crystals do not conduct electricity in solid state.

Ans. Conduction of electricity

(a) In solid state

In solid state, ionic crystals do not conduct electricity because on account of electrostatic force existing between them. The cations and anions remain tightly held together and hence occupy fixed positions.

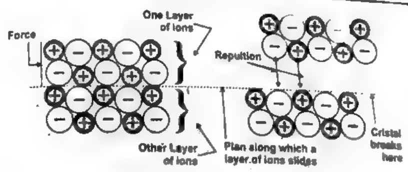
(b) In solution or in molten state

Ionic crystals conduct electricity when they are in solution or in the molten state. In both cases ions become free.

Q.12 (xiv) Ionic crystals are highly brittle.

Ans. Brittleness

Ionic solids are highly brittle because ionic solids are composed of parallel layers, which contain cations and anions in alternate positions, so that the opposite ions in the various parallel layers lie over each other. When an external force is applied, one layer of ions slides a bit over the other layer along a plane. In this way, the like ions come in front of each other and hence begin to repel. So, the application of little external force develops repulsion between two layers causing brittleness.



(viii) Density

Ionic solids are mostly of high density due to close packing of ions.

(ix) Ionic reactions

Such compounds having the ionic crystals give ionic reactions in polar solvents and these are very fast reactions

(x) Isomorphism and polymorphism

The properties like isomorphism and polymorphism are also associated with the ionic crystals

Q.12 (xv) The number of +ve ions surrounding the –ve ions in ionic crystal lattice depends upon the sizes of two ions.

Ans. In ionic compounds, negative ions are surrounded by positive ions or vice versa. Usually, each ion is surrounded by largest possible number of oppositely charged ions. The number of ions surrounding a particular ion depends upon radius ratio.

$$\text{Radius ratio} = \frac{\text{Radius of cation }(r+)}{\text{Radius of anion }(r-)}$$

Greater the radius ratio, greater is the coordination number. A greater surface area of an ion will have a tendency to get surrounded by large number of oppositely charged ions

Radius Ratio	Coordination number	Structure
0.155 – 0.225	3	Triangular
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	6	Octahedral
0.732 – 1.00	8	Cubic

Q.7(a) Explain the structure of NaCl. Sketch a model to justify that unit cell of NaCl has four formula units in it.

Structure of Sodium Chloride

The structure of ionic crystals depends upon the structure and the size of ions. Each ion is surrounded by a certain number of ions of opposite charge. In the structure of NaCl, each Na^+ ion is surrounded by six chloride Cl^- ions. These ions are arranged in a crystal lattice. Na^+ has ten electrons while Cl^- has total eighteen electrons. The size of Cl^- is bigger than that of Na^+.

Distance between ions

The distance between two nearest ions of same kind i.e., Cl^- ions is 5.63A°. The distance between two adjacent ions of different kind is 5.63/2 = 2.815 A°. The location of Na^+ and Cl^- ions is such that each Na^+ is surrounded by six Cl^- placed at the corners of regular octahedron.

Coordination number

"Coordination number of an ion is equal to number of ions surrounding that ion

Coordination number of each Na^+ is six similarly each Cl^- ion is also surrounded by six Na^+ ions

Na^+ and Cl^- are not connected to each other by pairs because all six Cl^- ions are at same distance away from one Na^+. The independent molecules of NaCl do exist in vapour phase. Anyhow, in solid NaCl, there are no independent molecules of NaCl. That's why sodium chloride is said to have formula unit of NaCl.

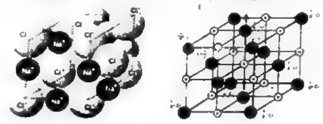
Cubic structure

There are eight Cl^- ions at the corners of the cube and each is being shared amongst eight cubes. 1/8th part of each Cl^- ion is considered for this unit cell. So one complete Cl^- is contributed by eight corners.

Similarly, six chloride ions are present at the face centres and each is being shared by two cells

Number of ions and formula units per unit cell

Per unit cell, there are 8/8 + 6/2 = 4Cl^- ions. If we take a unit cell having 8Na^+ at eight corners and 6Na^+ at faces. So there are equal number of Na^+ ions and therefore 4NaCl formula units are present per unit cell.



(a) (b)

The unit cell of sodium chloride showing that NaCl formula units are present in a unit cell.

Q10. What is coordination no. of an ion? What is coordination no. of cation in a (a) NaCl structure and (b) CsCl structure? Explain reason for this difference?

Ans. **Coordination number:** "The number of oppositely charged ions around an ion is called its coordination number."

- It depends upon radius ratio of cation and anion. In "NaCl" the radius ratio is between (0.414 - 0.732) so, Na^+ has a coordination number of '6' and its crystal is face centered cube where six Cl^- ions surround each Na^+ ion.
- In "CsCl" the radius ratio is 0.933 which lies between 0.732 and 1.00, so coordination number of Cs is '8' and its crystal is body centered cube where 8Cl^- ions surround each Cs^+ ion.

Lattice energies of ionic compounds

Ionic compound	Lattice energy ($kJ\ mol^{-1}$)
LiCl	-833
NaF	-895
NaCl	-787
KCl	-690
NaBr	-728
KBr	-665
NaI	-690

Lattice Energy

"The energy released when one mole of the ionic crystal is formed form the gaseous ions or the energy required to break one mole of solid into isolated ions in the gas phase is called lattice energy."

Explanation

Lattice energy decreases with the increase in the size of the cation keeping the anion same. It also decreases with the increase in the size of anion. The reason in both cases is the same. With the increase in the size of either cation or anion, the packing of oppositely charged ions becomes less and less tight.

Compound	Lattice enthalpy/$kJ\ mol^{-1}$	Ions	Effect of size of halide ion
NaCl	-787	⊕ ⊖	ionic size increases: • charge density decreases • attraction between ions decreases • lattice energy becomes less negative.
NaBr	-728	⊕ ⊖	
NaI	-690	⊕ ⊖	

Na^+	Mg^{2+}	Al^{3+}	P^{3-}	S^{2-}	Cl^-

With increased charge on cation, two factors increase the magnitude of lattice energy. • increased charge produces **more attraction** • decreasing size produces **more attraction.**	With increased charge on anion there are two competing factors. • from Cl^- to P^{3-}, the increasing ionic charge produces more attraction • however, the ionic size also increases producing less attraction

Q.7 (b) What are covalent solids? Give their properties.

Covalent Solids

"Those crystalline solids which consists of atoms of same or different elements held together through covalent bonds are called covalent solids."

- Covalent solids are also called atomic solids.

Examples

Diamond, graphite SiC, BN, etc.

Types of covalent solids

Covalent solids are of two types:

(i) Giant Structure Covalent Solids

When the covalent bonds join to form giant molecules.

e.g. diamond, silicon carbide, aluminium nitride.

(ii) Layered Structure Covalent Solids

When the atoms join to form the covalent bonds and separate layers are produced.

e.g. cadmium iodide, graphite, boron nitride.

Properties of Covalent Crystals

(i) Three dimensional open structure

The bonding in covalent crystals extend in three dimensions. They contain a network of atoms. The valencies of atoms are directed in definite directions. So the packing of atoms in these crystals is looser than those of ionic and metallic crystals. Thus covalent crystals have open structure.

(ii) Hardness, volatility, melting and boiling points

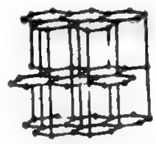
These crystals are very hard and considerable amount of energy is required to break them. They have high melting and boiling points and their volatility is very low.

(iii) Conduction

Due to the absence of free electrons and ions they are bad conductors of electricity.

Graphite is a conductor

In graphite, each carbon atom is sp^2 hybridized. Three out of four electrons of a carbon atom form covalent bond with neighbouring atoms. Thus a hexagonal layered structure of graphite is formed and the electrons are available between the layers. These electrons are delocalised and conductivity becomes possible. Graphite is not a conductor perpendicular to the layers.



Structure of graphite

(iv) Solubility

- Mostly covalent crystalline solids are insoluble in polar solvents like water.
- They are readily soluble in non-polar solvents like benzene and carbon tetrachloride.

- The covalent crystals having giant molecules like diamond and silicon carbide are insoluble in all the solvents. Because of their big size, they do not interact with the solvent molecules. The chemical reactions of such crystalline solids are very slow.

Structure of Diamond

Diamond is one of the allotropic modifications of carbon. Carbon has four electrons in its outermost shell. The four atomic orbitals (one 2s and three 2p) undergo sp^3 hybridization to give four sp^3 hybridized orbitals. They are directed in space along the four corners of tetrahedron.

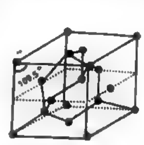
Tetrahedral unit in carbon atoms in diamond crystal

This is the unit cell of diamond and a larger number of such unit cells undergo sp^3–sp^3 overlapping to form a huge structure. Each carbon atom is linked with four other carbon atoms. The bonds between carbon atoms are covalent which run through the crystal in three dimensions. All the bond angles are 109.5° and the bond lengths are 154 pm. The whole lattice is, therefore, continuous and because of continuity of C–C covalent bonding, the entire diamond crystal behaves as a huge or giant three dimensional carbon molecule. This is also called "macromolecule".
The overall structure of diamond looks face-centred cubic.

Structure of diamond crystal

(ii) Diamond is hard and an electrical insulator.

Ans. Diamond is hard because C-C single bonds are very strong. A diamond crystal is composed of a network of carbon atoms extending uniformly throughout the entire crystal. In this three-dimensional network of atoms, each carbon atoms share its four valence electrons with four other carbon atoms to form four single bonds. The bonding atoms are tightly bound and highly localized. The network of atoms joined by strong tetrahedrally oriented covalent bonds is responsible for the hardness of diamond. As a result of strength and uniformity of the bonds, stable and rigid crystal lattice, diamond is hardest substance.
Diamond is electrical insulator because there are no free valence electrons. All the valence electrons are tightly bound and highly localized due to formation of four covalent bonds.



Face-centered cubic structure of diamond

Q.7 (c) What are molecular crystals? Give their properties. Justify that molecular crystals are softer than ionic crystals.

Molecular Solids

"Those solid substances in which the particles forming the crystals are polar or non-polar molecule or atoms of a substance are called molecular solids."

Types of attractive forces

Two types of intermolecular forces hold them together:
(i) Dipole-dipole forces
(ii) van der Waals's forces

These intermolecular forces are much weaker than the forces of attraction between the cations and the anions in ionic crystals and between the atoms in covalent crystals.

Types of Molecular Solids

(i) Molecular solids containing polar molecules

They have high melting and boiling points and less volatile and are soluble in water.
e.g. Ice, sugar etc.

(ii) Molecular solids containing non polar molecules

They have low melting and boiling points. They are soluble in non-polar solvents and are more volatile.
e.g. Iodine (I_2), Phosphorous (P_4), Carbon dioxide (CO_2) in solid state, Sulphur (S_8) etc.

Properties of molecular solids

(i) Regular arrangement

X-rays analysis has shown the regular arrangements of atoms in the constituent molecules of these solids and we get the exact positions of all the atoms.

(ii) Softness

The forces, which hold the molecules together in the molecular crystals, are very weak. So they are soft and easily compressible.

(iii) Volatility, melting and boiling points

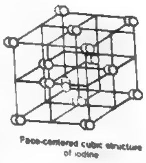
They are mostly volatile and have low melting and boiling points.

(iv) Conduction, solubility and density

They are bad conductors of electricity, have low densities and sometimes transparent to light. Polar molecular crystals are mostly soluble in polar solvents, while non-polar molecular crystals are usually soluble in non-polar solvents.

Structure of solid iodine

In solid state, the molecules of iodine align in the form of layer lattice. I-I bond distance is 271.5 pm and is appreciably longer than in gaseous iodine (266.6 pm). As expected from its structure, iodine is a poor conductor of electricity.



Face-centered cubic structure of iodine

(iv) Iodine dissolves readily in tetrachloromethane.

Ans. The general rule of solubility is "Like dissolves like". Non-polar solutes dissolve in non-polar solvents. Since both iodine (I_2) and carbon tetrachloride (CCl_4) are non-polar substances, so both dissolve into each other. The process [illegible] the breakdown of weak van der Waals forces in iodine lattice.

Metallic Solid

"Those crystals in which metal atoms are held together by metallic bonds are called metallic solids."

Metallic bond

"The attractive force which binds a metal cation to a number of electrons within its sphere of influence is called metallic bond."

Q.8 (a) Give different theories of a metallic bond. How electron sea theory does justifies the electrical of a metallic bond. How electron sea theory does justify the electrical conductivity, thermal conductivity and shining surface of metals?

Theories about Metallic Bond

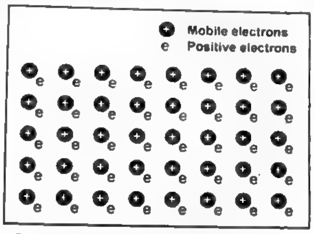
1. Electron pool or electron gas theory

This was proposed by Drude and extended by Loren in 1923. According to this theory:

"Each atom in a metal crystal loses all of its valence electrons. These valence electrons form a pool or a gas. The positively charged metal ions are believed to be held together by electron pool or gas."

Explanation

Due to low ionization energy, metal loses electrons and forms positively charged ions. These positively charged ions occupy definite positions at measurable distances from each other in the crystal lattice. Valence electrons are not attached to any individual ion or a pair of ions rather belong to the crystal as a whole. These electrons are free to move about from one part of the crystal to other. The force, which binds a metal cation to a number of electrons within its sphere of influence, is called metallic bond.



Positive ions surrounded by mobile electrons

2. Valence bond theory

Louis Pauling tried to explain metallic bond according to valence bond theory. According to this theory,
"The metallic bond is treated essentially as covalent in character. However, it is assumed that the covalent bonds are not localized but are highly delocalized in metal structure"

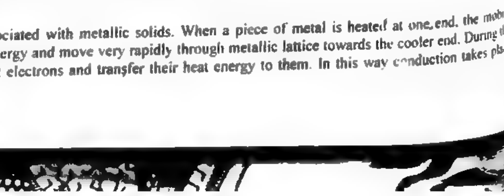
3. Molecular orbital theory

Recently, molecular orbital theory was applied to explain the characteristics of metallic solids. According to this theory, it is assumed that electrons in the completely filled orbitals are essentially localized, while atomic orbitals containing valenee electrons interact or overlap to form a set of delocalized orbitals. These delocalized orbitals are the molecular orbitals which extend over the entire crystal lattice. Such a combination of atomic orbitals produce as a large number of closely spaced states. These states of energy are also known as bands of energy. That is why it is also called a **band theory**. The energy gap between two bands determines the properties of the metallic solids

Properties of Metallic Crystals

Electrical conductivities of metals

Metals are good conductor of electricity. When electric field is applied between two ends of a metal then mobile electrons begin to move towards the positive pole and the new electrons from the negative pole take their place



Electrical conductivity of a metal

Effect of temperature on electrical conductivities of metals

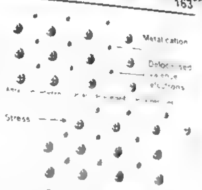
The electrical conductivities of metals decrease with the increase in temperature. The reason is that with the increase in temperature the positive metal ions also begin to **oscillate**, their amplitude increases and the motion hinders **the free movement of mobile electrons** between the positive ions. This hindrance decreases the electrical conductivity

Thermal conductivity

It is another property associated with metallic solids. When a piece of metal is heated at one end, the mobile electrons at this end absorb heat energy and move very rapidly through metallic lattice towards the cooler end. During the process, they collide with adjacent electrons and transfer their heat energy to them. In this way conduction takes place through one end to the other

Metallic luster

Whenever the metals are freshly cut, most of them possess metallic luster which means that they have a shinning surface. When light falls on the metallic surface, the incident light collides with the mobile electrons and they are excited. These electrons when de-excited give off some energy in the form of light. This light appears to be reflected from the surface of the metal which gives a shining look



Deformation of metal structures

Malleability and ductility

Metals are malleable and ductile whenever stress is applied on them. Their layers slip pass each other. The structure of the metal changes into wires and sheets without fracturing when stress is applied on them.

Q.12 (i) Sodium is softer than copper, but both are very good electrical conductors

Ans. The hardness of a metal is directly proportional to the strength of metallic bond, stronger the metallic bond harder is the metal and vice versa. The strength of metallic bond is directly proportional to number of valence electrons but inversely proportional to the size of metallic radius. Cu has greater number of valence electrons as compared to Na. So, the metallic bond of Na is weaker than Cu and it is relatively soft.

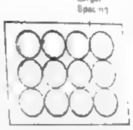
As, both Na and Cu have free valence electrons. Hence, both Na and Cu are very good electrical conductors

Q.12 (xi) The electrical conductivity of metals decrease by increasing temperature.

Ans. The electrical conductivity of metals decrease by increasing temperature because with the increase in temperature, the positive metal ions begins to oscillate and the motion hinders the free movement of mobile electrons between the positive ions. This hindrance decreases the electrical conductivity

Structure of Metals

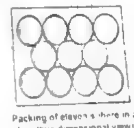
The metal atoms are arranged in definite pattern. Free electrons are roaming about in the crystal lattice. So a metal may be regarded as an assembly of the positively charged spheres of identical radii which are packed together to fill the space as completely as possible



Packing of twelve sphere in a box (two dimensional view)

Close packing of atoms

Let us suppose that the metal atoms are like hard spherical balls. Take twelve spherical balls and pack in a box as shown in Fig (a). The spaces during the packing are larger. When the box is shaken, the balls will rearrange as shown in Fig (b). The arrangement of these balls is now stable and more closely packed. It is the natural tendency of the balls to have closely packed arrangement of eleven spheres after shaking.



Packing of eleven sphere in a box (two dimensional view)

Development of unit cells of the crystal lattice

Consider three balls which join together in one plane. The fourth ball is inserted in the space created by the other three as a second layer. In this way tetrahedral structure is obtained Fig (c). Actually, the fourth ball of the second layer is placed in the depression created by the first three balls. These depressions are also called interstices or crevices or voids

The formation of a tetrahedral site due to four balls

Q. 8 (b) Explain with the help of a diagram
(i) Cubic close packing in the structure of metals
(ii) Hexagonal close packing in the structure of metals.

Ans. Structure of metals

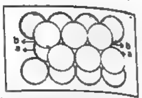
Consider eleven balls are present in the first layer. The balls of second layer can fit into the depressions or interstices created by the first layer. When the balls of the second layer are arranged, then all the depressions of first layer are not occupied. There are two types of depressions as 'a' and 'b'. The depressions marked 'b' are not occupied

by the second layer and one can see the ground from looking at the top through depressions 'b'. The new depressions marked 'a' are created by second layer. Through the depressions 'a', we cannot see the ground, but balls of the first layer

Now arrange the balls of third layer in the depression of second layer

When the balls of the third layer are placed above the second layer then there are two possibilities.

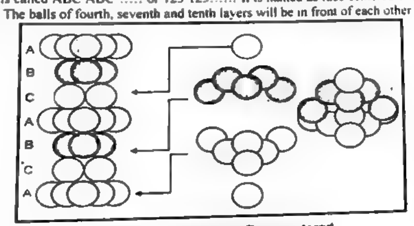
- The third layer balls may be accommodated in 'a' type interstices or depressions
- The third layer balls may be accommodated in 'b' type interstices or depressions



Close packing of spheres showing 11 balls in first layer and 6 balls in second layer

Cubic close packing

When the atoms of third layer fit into the interstices marked 'b', then atoms of the third layer will not lie directly above those of the atoms of first layer. This pattern of arrangement is called ABC ABC ..... or 123 123...... It is named as face centered cubic arrangement. The balls of fourth, seventh and tenth layers will be in front of each other



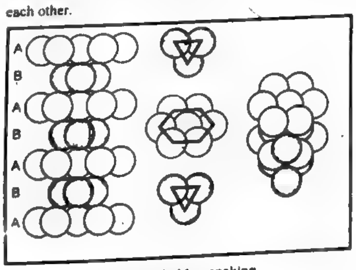
Cubic close packing or Face centered cubic arrangement (ABCABC ...)

Metals with a face centered cubic structures are generally most malleable and ductile. Body-centered cubic metals are intermediate, and hexagonal close-packed structures are least -malleable and ductile

Hexagonal close packing

When the atoms of the third layer are arranged in such a way that they occupy the depressions created by second layer i.e., in the 'a' types crevices then these atoms will directly lie above the atoms of first layer. This pattern of arrangement is usually written as ABAB.... .or 1212......

This pattern has been named as hexagonal close packing. The balls of third, fifth and seventh layers will be in front of each other.



Hexagonal close packing (ABAB ...)

Metals	Structure
Mg, Zn, Mo, V, Cd	hcp
Cu, Ag, Au, Ni, Pt	ccp or fcc
Li, Na, K, Rb, Cs, Ba	bcc

Q.12 (xii) In the closest packing of atoms of metals, 74% space is occupied.

Ans. Each atom in close packing is surrounded by six other atoms. Packing of atoms in this way gives a lattice where 74% space is occupied, where 26% forms crevices or interstices as free spaces

Type of Crystalline Solids

Type of Solid	Structural Particles	Intermolecular Forces	Typical Properties	Examples
metallic	cations plus delocalized electrons	metallic bonds	hardness varies from soft to very hard, melting points varied from low to very high, lustrous, ductile malleable, very good conductors of heat and electricity	Na, Mg, Al, Fe, Zn, Cu, Ag, W
ionic	cations and anions	electrostatic attractions	hard, moderate to very high melting points, non-conductors of electricity (but good electrical conductors in the molten state)	NaCl, $NaNO_3$, MgO
molecular	molecules (atoms of noble gases)	London and / or dipole-dipole and / or hydrogen bonds	soft, low melting points, non-conductors of heat and electricity, sublime easily in many cases	noble-gas elements, CH_4, CO_2, P_4, S_8, I_2, H_2O
network covalent	atoms	covalent bonds	very hard, very high melting points non-conductors of electricity	C (diamond) SiC, SiO_2

(v) The vapour pressures of solids are far less than those of liquids.

Ans. The magnitude of vapour pressure is inversely proportional to the strength of intermolecular attractive forces These forces are stronger in solids as compared to the liquids. Hence, vapour pressure of solids is far less than liquids

Determination of Avogadro's Number (N_A)

Avogadro number can be calculated in a number of different ways. One of the most accurate methods for determining this number is based on the study of crystalline solids. In order to calculate this number, we need to know the volume of one gram-mole of a crystalline solid and the distance between its atoms or ions in the crystal lattice. The volume of one gram –mole of a solid can be calculated from its density while the spacing between its atoms can be measured by X-rays.

The method of determining Avogadro's number is explained with a help of following solved example which gives a reasonable good value of this number. The crystal of LiF is primitive cube and can be used to calculate the Avogadro's number

Example

The density of LiF is 2.65 g cm^{-3}. It is made up of cubic array of alternate Li^+ and F^- ions and the distance between these ions is $2.01\,\mathring{A}\,(2.01\times10^{-8}\,cm)$. Calculate the Avogadro's number.

Solution

The formula mass of LiF $= 6.939 + 18.9984$

$= 25.9374\ g\ mol^{-1}$

Density of LiF $= 2.65\ g\ cm^{-3}$

From the density and molar mass, calculate the volume of 1 mole of solid LiF

The volume occupied by one formula unit of LiF $= \dfrac{25.9374\,g\,mol^{-1}}{2.65\,g\,cm^{-3}}$

$= 9.788\,cm^3\,mol^{-1}$

From this volume, we can calculate the edge length of the cube.

For this, we suppose that $9.788\,cm^3$ of LiF i.e., 1 mole of LiF, is present in the form of a cube. The cube root of this volume will give the length of one edge of cube

$$\text{Edge length of the cube} = \sqrt[3]{9.788\,cm^3}$$
$$= 2.139\,cm$$

The number of ions of both Li^+ and F^- on one edge length can be calculated by dividing the edge length by distance between ions

Hence, the number of $(Li^+ \text{ and } F^-)$ ions along one edge length

$$= \frac{2.139\,cm}{2.01\times10^{-8}\,cm\,ion^{-1}}$$
$$= 1.064\times10^{8}$$

When we take cubes of these ions we get the total number of ions i.e., Li^+ and F^- in the cube

$$\text{Total number } (Li^+F^-) \text{ of ions in the cube} = (1.064\times10^{8})^3$$
$$= 1.204\times10^{24}$$

Since the cube of LiF crystal contains one Avogadro's number of Li^+ and one Avogadro's number of F^-, so the Avogadro's number will be

$$= \frac{1.204\times10^{24}}{2} = 6.02\times10^{23}$$

KEY POINTS

1. In crystalline solids the particles are arranged in a regular and repeating manner. The essential structural features of a crystalline solid can be represented by its unit cell. The three dimensional array of points representing atoms, ions or molecules is called crystal lattice. The points in the crystal lattice represent positions in the structure where they have identical environments.
2. The simplest unit cell is a cubic unit cell. There are seven crystal systems overall.
3. The properties of solids depend on the arrangement of particles and the attractive forces between them. Ionic solids are hard and brittle and have high melting points. Cavalent solids consist of atoms held together by covalent bonds and these bonds extend throughout the solid. They are hard and have high melting points. Metallic solids consist of metal cations immersed in a sea of electrons and give a wide range of properties. Molecular solids consist of atoms or molecules held together by intermolecular forces.

Solved Objective Exercise

Q1. Multiple choice questions:

(i) Ionic solids are characterized by
- (a) low melting points
- (b) good conductivity in solid state
- (c) high vapour pressure
- (d) solubility in polar solvents

(ii) Amorphous solids
- (a) have sharp melting points
- (b) undergo clean cleavage when cut with knife
- (c) have perfect arrangement of atoms
- (d) can possess small regions of orderly arrangement of atoms

(iii) The molecules of CO_2 in dry ice form the
- (a) ionic crystals
- (b) covalent crystals
- (c) molecular crystals
- (d) any type of crystal

(iv) Which of the following is a pseudo solid?
- (a) CaF_2
- (b) Glass
- (c) NaCl
- (d) All

(v) Diamond is a bad conductor because
- (a) it has a tight structure
- (b) it has a high density
- (c) has no free electron in crystal
- (d) is transparent to light

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(d) solubility in polar solvents	Ionic solids have high melting points, non conductors of electricity in solid state, low vapour pressure and soluble in polar solvents like water
(ii)	(d) can possess small regions of orderly arrangement of atoms	Amorphous solids do not have sharp melting points. They do not possess a regular orderly arrangement of particles
(iii)	(c) molecular crystals	When CO_2 gas is cooled at –78°C it converts into solid state called dry ice. In solid state it consists of CO_2 molecules
(iv)	(b) Glass	Pseudo solid is also called amorphous solid. Glass, Paper, Glue, wood, Plastic rubbers etc are its examples
(v)	(c) has no free electron in crystal	In diamond, carbon is sp^3 hybridized. All four valence electrons are busy in bond formation with neighbouring C – atoms. No electron is available to conduct the electricity

Q2. Fill in the blanks:

(i) In a crystal lattice, the number of nearest neighbours to each atom is called the ________

(ii) There are ________ Bravis lattices

(iii) A pseudo solid is regarded as a ________ liquid

(iv) Glass may begin to crystallize by a process called ________

(v) Crystalline solids which exhibit the same ________ in all directions are called ________

(vi) The branch of science which deals with ________ of crystals is called crystallography

ANSWERS

(i) coordination number	(ii) fourteen
(iii) super cooled	(iv) annealing
(v) physical properties, isotropic	(vi) structure

Q3. Indicate 'true' or 'false' as the case maybe.

(i) There are five parameters in unit cell dimensions of a crystal

(ii) Ionic crystals are very hard, low volatility and very low melting and boiling points

(iii) The value of lattice energy of the ionic substances depends upon the size of ions

(iv) Molecular orbital theory of solids is also called band theory.
(v) Ionic solid is good conductor of electricity in the molten state.

ANSWERS

(i) False	(ii) False	(iii) True	(iv) True	(v) True

Additional Questions

Q. The lattice energy of NaCl is greater than KCl. Why?

Ans. The lattice energy of ionic compounds depends upon the charge density of oppositely charged ions. Greater the charge density of ions, greater will be the lattice energy. The anion in both NaCl and KCl is same (Cl^-), but cation is different. Both Na^+ and K^+ ions carry same charge but the size of Na^+ is small than K^+. Due to which charge density of Na^+ ion is greater than that of K^+ (Since, charge density is the charge to size ratio of ion). As a result, the lattice energy of NaCl is greater than KCl.

Q. Why metals are changed into wires and sheets by applying the stress?

Ans. Malleability means beaten into sheet and ductility means drawn into wires. These properties are due to the non-directional nature of the metallic bond. When any force is applied on the metal the position of the cations is changed without destroying the crystal. The metallic lattice gets deformed due to the slippage of the adjacent layers of the cations from one part to another It doesn't change the environment of the cations. It simply moves the cations from one lattice to another

Q. Why does Iodine sublime.

Ans. Iodine is held by the weakest van der Waals's attractions because it is a covalent nonmetal substance. Iodine also has low vapor pressure Once Iodine reaches a certain point, there's not enough force holding the molecules together to even make a liquid. Instead, they escape and become a gas.

Important Previous Board Questions

Q. I-I bond distance in solid iodine is longer than in gaseous iodine. Justify.
Q. Metals are good conductor of heat and electricity. Justify.
Q. Why the electrical conductivity of metals decreases with increase in temperature?
Q. A freshly cut metal has a lustrous surface. Give reason.
Q. Why cleavage of crystals is itself anisotropic behavior?
Q. Molecular solids are soft and easily compressible. Why?
Q. How the amount of lattice energy of an ionic compound depends upon the charge densities of the ions?

For Answers study Scholar's CHEMISTRY (Objective) XI

Chapter 5

ATOMIC STRUCTURE

Sub Atomic Particles of Atom

Matter is made up of extremely small particles called atoms. According to Dalton's theory, atoms were considered to be ultimate particles which could not be divided any further Our ideas about structure of atom have undergone radical changes over the years. A number of subatomic particles have been discovered.

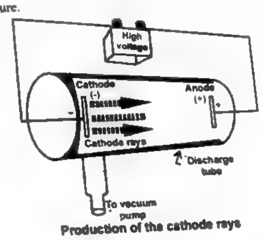
DISCOVERY OF ELECTRONS (Cathode Rays)

Apparatus

- A gas discharge tube is fitted with two metallic electrodes acting as cathode and anode.
- The tube is filled with a gas, air or vapours of a substance at any desired pressure
- The electrodes are connected to a source of high voltage. The exact Voltage required depends upon

(i) Length of the tube
(ii) Pressure inside the tube

- The tube is attached to a vacuum pump by means of a small side tube so that the conduction of electricity may be studied at any value of low pressure.



English = 85
MATHS 100
CHEMIST - 50
Urdu : 80
Islam = 45
Physics 95

Production of the cathode rays

Working

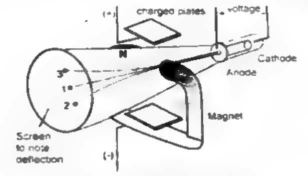
It is observed that current does not flow through the gas at ordinary pressure even at high voltage of 5000 volts When the pressure inside the tube is reduced and a high voltage of 5000-10000 volts is applied, then an electric discharge takes place through the gas producing a uniform glow inside the tube. When the pressure is reduced further to about 0.01 torr, the original glow disappears Some rays are produced which create fluorescence on the glass wall opposite to the cathode These rays are called cathode rays. The colour of the glow or the fluorescence produced on the walls of the glass tube, depends upon the composition of glass.

Properties of Cathode Rays

(i) Effect of electrical and magnetic fields

Cathode rays are negatively charged. In 1895, J. Perrin showed that when the cathode rays passed between the poles of the magnet, the path of the negatively charged particles was curved downward to the point 2 by the magnetic field.

In 1897, J. Thomson established their electric charge by the application of electric field, the cathode rays particles were deflected upward (towards the positive plate) to point 3



Deflection of cathode rays in electric and magnetic fields

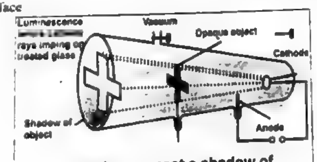
Thomson found that by carefully controlling the charge on the plates when the plates and the magnet were both around the tube, he could make the cathode rays strike the tube at point 1 again. In other words, he was able to cancel the effect of the magnetic field by applying the electric field that tended to bend the path of the cathode rays in the opposite direction.

(2) Fluorescence

They produce a greenish fluorescence on striking the walls of the glass tube. These rays also produce fluorescence in rare earths and minerals. When placed in the path of these rays, **alumina glows red and tin stone yellow.**

(3) Straight line motion

They cast a shadow when an opaque object is placed in their path. It proves that they travel in a straight line perpendicular to the cathode surface.



Cathode rays cast a shadow of an opaque object

(4) Material Particles

These rays can drive a small paddle wheel placed in their path. This shows that these rays possess momentum. It is also concluded from this experiment that cathode rays are not rays but material particles having a definite mass and velocity.

(Cathode rays derive a small paddle wheel)

(5) X-rays production

Cathode rays can produce X-rays when they strike an anode particularly with large atomic mass.

(6) Heating effect

These rays can produce heat when they fall on matter, e.g. when cathode rays from a concave cathode are focused on a platinum foil, it begins to glow.

(7) Ionization

They can ionize gases through which they pass.

(8) Penetration

They can pass through a thin metal foil like aluminum or gold foil.

(9) Reducing effect

They can cause a chemical change, because they have a reducing effect.

(10) The nature of the cathode rays does not depend upon the nature of the cathode material or the nature of the gas filled in the discharge tube.

(11) e/m value

The e/m value of cathode rays shows that they are simply electrons.

The negatively charged particles were called negatrons by Thomson which was changed to electrons by stoney.

Conclusion

- J.J. Thomson concluded from his experiments that cathode rays consist of streams of negatively charged particles.
- Stoney named these particles as electrons.
- Thomson also determined the charge to mass ratio (e/m) of electrons. He found that the e/m value remains the same no matter which gas was used in the discharge tube. He concluded that electrons are the fundamental particles of matter.

Q4a. Why is it necessary to decrease the pressure in the discharge tube to get cathode rays?

Ans. At normal pressure, the gas molecules are congested in discharge tube. When the pressure inside the tube is reduced to decrease the number of gas molecules so that hindrance in the way of movement of electrons of cathode rays become minimized. At a pressure of 0.01 torr, the molecules are very isolated and apart from each other. This creates a conducting medium for the passage of cathode rays.

Q4b. Whichever gas is used in the discharge tube, the nature of the cathode rays remains same. Why?

Ans. J.J Thomson concluded from his experiments that cathode rays consist of streams of negatively charged particles. He also determined the charge to mass ratio of electrons that is 1.7588×10^{11} coulombs kg^{-1}. He performed many experiments by using different gases in discharge tube and found that the e/m value for cathode rays remained the same no matter which gas was used in the discharge tube. Thomson concluded that all atoms contained electrons. This show that whichever gas is used in the discharged tube, the nature of the cathode rays remains the same.

Q4c. Why e/m of cathode rays is equal to that of electron?

Ans. In 1897, J.J. Thomson by a series of experiments determined the e/m value of particles of cathode rays. It was found to be -1.7588×10^{11} C kg^{-1}. This value was exactly same as that of e/m value of electron. So it was concluded that cathode rays are stream of negatively charged particles called **electrons**.

Q4d. How the bending of the cathode rays in the electric and magnetic fields shows that they are negatively charged?

Ans. In the absence of any electric or magnetic field, cathode rays move in straight line perpendicular to the surface of cathode.

In 1895, J Perrin showed that when cathode rays are passed between the poles of the magnet, the cathode rays was deflected which showed that they have charge.

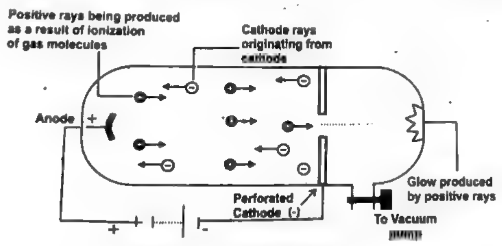
In 1897, Sir J.J Thomson established their electric charge by the application of electric field. The cathode rays deflected towards positive plate showing their negative nature.

DISCOVERY OF PROTON

In 1886, German physicist, **Eugene Goldstein** performed discharge tube experiment.

Apparatus

A discharge tube provided with a cathode having extremely fine holes in it. Such a cathode is called perforated cathode.



(Production of positive rays)

Working

When a large potential difference is applied between electrodes, it is observed that while cathode rays are travelling away from cathode, there are other rays produced at the same time. These rays after passing through the perforated cathode produce a glow on the wall opposite to the anode.

Canal rays or positive rays

Since these rays pass through the canals or the holes of cathode, they are called canal rays. These rays are named as positive rays owing to the fact that they carry positive charge.

Reason for the production of positive rays

These positive rays are produced due to the ionization of the gas molecules in the discharge tube. When high speed cathode rays (electrons) strike with the gas molecules, they knock out electrons from the gas molecules and positive ions are produced which start moving towards the cathode.

$$M + e^- \longrightarrow M^+ + 2e^-$$

Properties of Positive Rays

(1) Effect of electric and magnetic fields

They are deflected by electric and magnetic fields. This shows that these rays are positively charged.

(2) Straight line motion

These rays travel in a straight line in a direction opposite to the cathode rays.

(3) Produce flashes

They produce flashes in ZnS plate.

(4) e/m value

The e/m value for the positive rays is always smaller than that of electrons and depends upon the nature of gas used in the discharge tube. Heavier the gas, smaller is the e/m value.

Proton....a fundamental particle

e/m value will be maximum when discharge tube contains hydrogen gas because value of "m" is the lowest for the positive particle obtained from the hydrogen gas. Hence the positive particle obtained from hydrogen gas is the lightest among all the positive particles. This particle is called proton, a name suggested by Rutherford

The mass of a proton is 1836 times more than that of an electron.

Q46. Why positive rays are called canal rays?

Ans. E. Goldstein discovered positive rays by using a perforated cathode in discharge tube. He observed that not only cathode rays are formed in discharge tube but some rays after passing through the perforated cathode produce a glow on the wall opposite to anode. Since the rays pass through holes or canals of perforated cathode, they are called canal rays.

Q47. The e/m value of positive rays for different gases are different but those for cathode rays the e/m value are always same. Justify it.

Ans. As positive rays are formed by ionization of gas molecules inside the discharge tube, every gas has different nature of positive ion produced. Therefore e/m of positive rays depends upon nature of gas. Lighter the gas, greater the value of e/m and vice versa.

Whereas cathode rays are only electrons whose nature remains same whichever gas is used in discharge tube. So e/m value of cathode rays always remains same. No matter which gas is used

Q48. The e/m value for positive rays obtained from hydrogen gas is 1836 times less than that of cathode rays. Justify it.

Ans. The hydrogen atom contains only two fundamental particles i.e. one proton and one electron.

When hydrogen gas is used in the discharge tube, the positive rays particles are just protons and cathode rays particles are electrons. Since, a proton is 1836 times heavier than an electron, therefore e/m value for positive rays obtained from hydrogen is 1836 times lesser than that of cathode rays.

DISCOVERY OF NEUTRON

Proton and electron were discovered in 1886 and their properties were completely determined till 1895. It is very strange to know that upto 1932 it was thought that an atom was composed of only electrons and protons. Rutherford predicted in 1920 that some kind of neutral particle having mass equal to that of proton must be present in an atom, because he noticed that atomic masses of atoms could not be explained, if it were supposed that atoms had only electrons and protons.

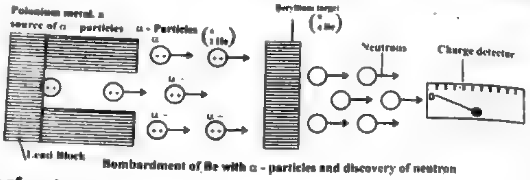
Chadwick discovered neutron in 1932 and was awarded Nobel prize in Physics in 1935.

Chadwick's experiment

A stream of α - particles produced from a polonium source was directed at beryllium $\left({}^9_4Be\right)$ target. It was noticed that some penetrating radiation were produced. These radiations were called neutrons because the charge detector showed them to be neutral. The nuclear reaction is as follows.

$$\underset{(\alpha\text{ - particle})}{{}^4_2He} + {}^9_4Be \rightarrow {}^{12}_6C + {}^1_0n$$

Actually α-particles and the nuclei of Be are re-arranged and extra neutron is emitted.



Bombardment of Be with α - particles and discovery of neutron

Properties of neutrons

(1) Free neutrons decay to produce a proton $\left({}^{1}_{+1}P\right)$ with the emission of an electron $\left({}^{0}_{-1}e\right)$ and a neutrino $\left({}^{0}_{0}n\right)$.

$${}^{1}_{0}n \rightarrow {}^{1}_{+1}P + {}^{0}_{-1}e + {}^{0}_{0}n$$

(2) Neutrons cannot ionize gases

(3) Neutrons are highly penetrating particles.

(4) Neutrons can knock out high speed protons from paraffin, water, paper and cellulose.

(5) When neutrons travel with an energy 1.2 Mev, they are called fast neutrons but with energy below lev are called slow neutrons Slow neutrons are usually more effective than fast ones for the fission purpose.

(6) When neutrons are used as projectiles, they can carry out the nuclear reactions. A fast neutron ejects an α – particles from the nucleus of nitrogen atom and boron is produced, alongwith an α – particles.

$${}^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{11}_{5}B + {}^{4}_{2}He$$

(7) When slow moving neutrons hit the Cu metal then γ radiations are emitted. The radioactive ${}^{66}_{29}Cu$ is converted into ${}^{66}_{30}Zn$

$${}^{63}_{29}Cu + {}^{1}_{0}n \rightarrow {}^{66}_{29}Cu + h\nu \quad (\gamma - \text{radiation})$$

$${}^{66}_{29}Cu \rightarrow {}^{66}_{30}Zn + {}^{0}_{-1}e$$

Actually, neutron is captured by the nucleus of ${}^{63}_{29}Cu$ and ${}^{66}_{29}Cu$ is produced. This radioactive ${}^{66}_{29}Cu$ emits an electron (β particle) and its atomic number is increases by one unit.

(8) Due to their intense biological effects, they are being used in the treatment of cancer.

(9) Neutron is not having any charge but it mass is 1.6750×10^{-27} kg or 1.0087 amu.

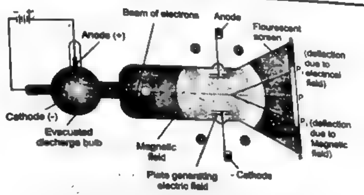
Fast Neutron	Slow Neutron
They travel with an energy of 1.2MeV.	They travel with an energy less than 1eV.
They are less effective in fission reaction.	They are more effective in fission reaction.
They mostly produce α-particles e.g. Reaction of fast neutron with ${}^{14}_{7}N$ ${}^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{11}_{5}B + {}^{4}_{2}He(\alpha - \text{Paticles})$	They produce β and γ-particles e.g. Reaction of slow neutron with ${}^{63}_{29}Cu$ ${}^{63}_{29}Cu + {}^{1}_{0}n \rightarrow {}^{66}_{29}Cu + h\nu(\gamma - \text{rays})$ ${}^{66}_{29}Cu \rightarrow {}^{66}_{30}Zn + {}^{0}_{-1}e(\beta - \text{rays})$

(b) What is J.J Thomson's experiment for determining e/m value of electron?

Measurement of e/m Value of Electron

Introduction

The e/m ratio of an electron was determined by J. J. Thomson using the following apparatus:



Measurement of e/m value of an electron by J.J. Thomson

Working

The cathode rays are allowed to pass through electric and magnetic fields When both the fields are off then a beam of cathode rays, consisted of electrons, produces bright luminous spot at P_1 on the fluorescent screen. The north and south poles of magnetic field are perpendicular to the plane of paper in the diagram. The electrical field is in the plane of paper. When only magnetic field is applied, the cathode rays are deflected in a circular path and fall at the point P_1. When only electric field is applied, the cathode rays produce a spot at P_2. Both electric and magnetic fields are then applied simultaneously and their strengths adjusted in such a way that cathode rays again hit the point P_1

Calculation

The value of e/m of cathode rays or electrons can be calculated by the following relationship

$$Hev = mv^2/r$$

or $He = mv/r$

or $e/m = v/Hr \quad (v = E/H)$

Hence $e/m = E/H^2r$

Where
- e = charge on electron
- m = mass of an electron
- v = velocity of electron
- r = radius of circular path of electron
- H = strength of magnetic field
- E = strength of electric field

Conclusion

From above experiment, it was concluded that e/m value of electron is 1.7588×10^{11} coulombs kg^{-1} This means that 1 kg of electrons have 1.7588×10^{11} coulombs of charge

Q.5 (a) Explain Millikan's oil drop experiment to determine the charge of an electron.

Measurement of Charge on Electron (Millikan,s Oil Drop Method)

In 1909, Millikan determined the charge on an electron by oil drop method

1. Instrumentation

(i) Metallic chamber

The apparatus consists of a metallic chamber. It has two parts. The chamber is filled with air, the pressure of which can be adjusted by a vacuum pump.

(ii) Electrodes

There are two electrodes A and A'. These electrodes are used to generate an electrical field in the space between the electrodes.

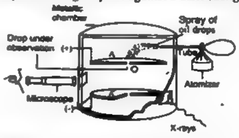
- The upper electrode is connected to positive terminal of the battery. It has a hole in it
- The lower electrode is connected to negative terminal of the battery

(iii) Atomizer

A fine spray of oil droplets is created by an atomizer. A few droplets passes through the hole in the top plate into the region between the charged plates

(iv) Microscope

One of the droplet is observed through a microscope. This droplet when illuminated perpendicularly to the direction of view, appears in the microscope, as a bright speck against a dark background.



Millikan's oil drop method for determination of charge of electron

2. Working

(i) In the absence of electric field

The droplet falls under the force of gravity without applying the electric field. The velocity of the droplet is determined. The velocity of the droplet (v_1) depends upon its weight, mg.

$v_1 \propto mg \quad \ldots(i)$

Where m = mass

g = acceleration due to gravity

(ii) In The Presence Of Electric Field

After that the air between the electrodes is ionized by X-rays. The droplet under observation takes up an electron and gets charged. Now, connect A and A' to a battery which generates an electric field having a strength E. The droplet moves upwards against the action of gravity with a velocity (v_2).

$v_2 \propto Ee - mg \quad \ldots(ii)$

Where 'e' is the charge on the electron and Ee is the upward driving force on the droplet due to applied electrical field of strength E.

3. Calculation

Dividing eq. (i) by (ii)

$$\frac{v_1}{v_2} = \frac{mg}{Ee - mg}$$

The values of v_1 and v_2 are recorded with the help of microscope. The factors like g and E are also known. Mass of the droplet can be determined by varying the electric field in such a way that the droplet is suspended in the chamber. Hence 'e' can be calculated.

4. Conclusion

By changing the strength of electrical field, Millikan found that the charge on each droplet was different. The smallest charge which he found was 1.59×10^{-19} coulombs, which is very close to the recent value of 1.6022×10^{-19} coulombs. The smallest charge on any droplet is the charge of one electron. The other drops having more than one electron on them, have double or triple the amount of this charge. The charge present on an electron is the smallest charge of electricity that has been measured so far

Evaluate the mass of an electron by the help of e/m and charge value.

Mass of electron

The value of charge on electron is 1.6022×10^{-19} coulombs, while e/m of electron is 1.7588×10^{11} coulombs kg^{-1} So,

$$\frac{e}{m} = \frac{1.6022 \times 10^{-19} \text{ coulombs}}{\text{Mass of electron}} = 1.7588 \times 10^{11} \text{ coulombs kg}^{-1}$$

Rearranging

$$\text{Mass of electron} = \frac{1.6022 \times 10^{-19} \text{ coulombs}}{1.7588 \times 10^{11} \text{ coulombs kg}^{-1}}$$

Mass of electron $= 9.1095 \times 10^{-31}$ kg

Properties of Fundamental Particles

	Electron	Proton	Neutron
(i) Discovery	J. J. Thomson	Eugene Goldstein	James Chadwick
(ii) Year	1886	1886	1932
(iii) Charge	-1.6022×10^{-19} C	$+1.6022 \times 10^{-19}$ C	Neutral
(iv) Mass (a) kg (b) a.m.u	 9.1095×10^{-31} kg 5.4858×10^{-4} amu	 1.6726×10^{-27} kg 1.0073 amu	 1.6750×10^{-27} kg 1.0087 amu
(v) Heavier than e^-	Equal	1836 times	1843 times

(b) Rutherford's atomic model is based on the scattering of α – particles from thin gold foil. Discuss it and explain the conclusions.

Rutherford's Atomic Model (Discovery of Nucleus)

Discovery

In 1911, Lord Rutherford discovered nucleus along with Marsden and Geiger Counter by performing a classic experiment.

$${}^{216}_{84}Po \longrightarrow {}^{212}_{82}Pb + {}^{4}_{2}He(\alpha\text{-particle})$$

Experiment

A beam of high speed α-particles emitted from a radioactive metal (radium or polonium) was directed onto a gold foil of 0.00004 cm thickness as target through a pin-hole in lead plate. A photographic plate or a screen coated with zinc sulphide was used as a detector.

Observation

Whenever, an α-particle struck the screen, a flash of light was produced at that point. From experiments, he observed that:

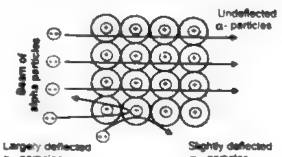
- Most of the particles went through the foil undeflected.
- Some were deflected at fairly large angles.
- A few were deflected backward.

Conclusion

Rutherford proposed that the rebounding particles must have collided with the central heavy portion of the atom which be called as nucleus.

Planetary model of an atom

On the basis of these experimental observations, Rutherford proposed the planetary model (similar to the solar system) for an atom in which a tiny nucleus is surrounded by an appropriate number of electrons. Atom as a whole being neutral, therefore, the nucleus must be having the same number of protons as there are number of electrons surrounding it.



(Rutherford's experiment for scattering of α - particles)

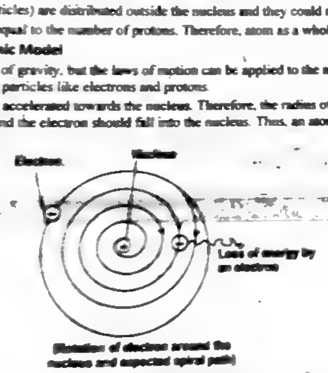
Postulates of Rutherford's atomic model

- Most of the α-particles go straight undeflected showing large area of atom is empty.
- Deflection of α-particles showed that some massive object is present in the centre of atom called nucleus.
- All the particles except electrons are present in the nucleus called nucleons.
- Electrons (extra-nuclear particles) are distributed outside the nucleus and they could not be stationary.
- The number of electrons is equal to the number of protons. Therefore, atom as a whole is neutral.

Defects of Rutherford's Atomic Model

(i) This model was based on law of gravity, but the laws of motion can be applied to the neutral particles like planets and are not applicable on charged particles like electrons and protons.

(ii) The moving electron must be accelerated towards the nucleus. Therefore, the radius of the orbiting electron should become smaller and smaller and the electron should fall into the nucleus. Thus, an atomic structure as proposed by Rutherford would collapse.



(Rotation of electron around the nucleus and expected spiral path)

(iii) The electron continuously revolves around the nucleus radiating energy, but its spectrum, instead of being continuous, is line spectrum.

PLANCK'S QUANTUM THEORY

Max Planck proposed the quantum theory in 1900 to explain the emission and absorption of radiation. The main points of revolutionary Planck's quantum theory are as follows:

(i) Energy is not emitted or absorbed continuously. Rather, it is emitted or absorbed in a discontinuous manner and in the form of wave packets. Each wave packet or quantum is associated with a definite amount of energy. In case of light, the quantum of energy is often called photon.

(ii) The amount of energy associated with a quantum of radiation is proportional to the frequency of radiation.

$$E \propto \upsilon$$
$$E = h\upsilon$$

Where h = Planck's constant and its value is 6.626×10^{-34} Js.

(iii) A body can emit or absorb energy only in terms of quanta.

$$E = h\upsilon$$
$$\upsilon = \frac{c}{\lambda}$$
$$E = \frac{hc}{\lambda}$$

Characteristics of Wave Motion

Frequency

"The number of waves passing through a point per second is called its frequency."

Symbol: Its symbol is υ.

Units: Its units are hertz, cycle/sec, revolution/sec.

Relation: It is inversely proportional to wavelength.

$$\upsilon \propto \frac{1}{\lambda}$$

Q. The frequency of the radiation having wave number $10\,m^{-1}$ is
(a) $10 s^{-1}$ (b) $3 \times 10^{7} s^{-1}$
(c) $3 \times 10^{11} s^{-1}$ (d) $3 \times 10^{9} s^{-1}$
[Ans. (d)]
[Hint: $\bar{\upsilon} = \frac{1}{\lambda}$]
$\upsilon = c\bar{\upsilon} = \frac{c}{\lambda} = 3 \times 10^{8} \times 10 = 3 \times 10^{9} s$

Wavelength

"The distance between the adjacent crests or troughs is called wavelength."

Units: Its units are Å, nm or pm.

Symbol: Its symbol is lambda. (λ)

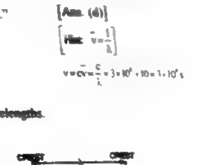
Relation: It is inversely proportional to frequency.

$$\lambda \propto 1/\upsilon$$

It tells us about the nature of radiation. Different radiations have different wavelengths.

Wave Number

"Number of waves per unit length is called wave number."



Units: Its units are cm^{-1}, m^{-1} etc.

Symbol: It is denoted by $\bar{\upsilon}$.

Relation: It is equal to the reciprocal of wavelength.

$$\bar{\upsilon} = \frac{1}{\lambda}$$

Relating energy of a photon to υ, $\bar{\upsilon}$ and λ

Putting the value of $\frac{1}{\lambda}$ in equation

$$E = \frac{hc}{\lambda}$$

We get $$E = hc\bar{\upsilon}$$

So greater the wave number of photon, greater is the energy associated with it.

Amplitude (a):

"It is the height of crest or depth of the trough of a wave."

- It is generally expressed by the letter 'a'.
- The amplitude of a wave determines the intensity of radiation.

Velocity (c):

The distance travelled by a wave in a second is called velocity of the wave.

- It is denoted by the letter c
- The frequency (ν) and wave length (λ) are related to velocity (c) by the relation . $c = \lambda \nu$ $\quad \nu = c/\lambda$
- Velocity of electromagnetic radiation in space or in vacuum is the same and is equal to $3 \times 10^8\ m\,s^{-1}$ or $3 \times 10^{10}\ cm\,s^{-1}$

Q.7 (a) Give the postulates of Bohr's atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

BOHR MODEL OF ATOM

Objectives

In order to remove defects in Rutherford model and to explain origin of spectral lines, Bohr introduced his atomic model

Base

This model was based on Planck's quantum theory.

The **main postulates** of Bohr's theory are:

(i) Electron revolves in one of the circular orbits outside the nucleus. Each orbit has a fixed energy and a quantum number is assigned to it.

(ii) Electron present in a particular orbit neither emits nor absorbs energy while moving in the same fixed orbits. The energy is emitted or absorbed only when an electron jumps from one orbit to another

(iii) When an electron jumps, the energy change ΔE is given by the Planck's equation

$$\Delta E = E_2 - E_1 = h\upsilon$$

(iv) Electron can revolve only in those orbits having a fixed angular momentum (mvr). The angular momentum of an orbit depends upon its quantum number and it is an integral multiple of the factor $h/2\pi$ i.e.

$$mvr = \frac{nh}{2\pi}$$

where n = 1, 2, 3, ...

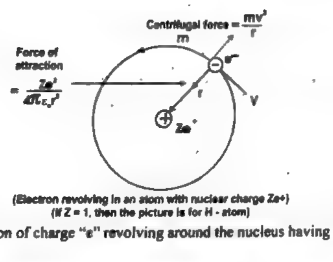
The permitted values of angular momenta are, therefore

$$\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$$

The electron is bound to remain in one of these orbits and not in between them. So angular momentum is quantitized.

(b) Derive the equation for the radius of n^{th} orbit of hydrogen atom using Bohr's model.

Derivation of Radius of Revolving Electron in nth Orbit



(Electron revolving in an atom with nuclear charge Ze+)
(If Z = 1, then the picture is for H - atom)

For a general atom, consider an electron of charge "e" revolving around the nucleus having charge Ze^+

Let
Mass of an electron = m
Velocity of the revolving electron = v
Radius of orbit = r

According to Coulomb's law, the electrostatic force of attraction between nucleus and electron is given as

$$\text{Electrostatic force} = \frac{Ze^2}{4\pi\epsilon_o r^2} \quad ...(i)$$

$$\frac{Ze^+ . e^-}{4\pi\epsilon_o r^2} = \frac{Ze^2}{4\pi\epsilon_o r^2}$$

where ϵ_o is the permittivity in vacuum and has a value of $8.84 \times 10^{-12}\ C^2 J^{-1} m^{-1}$. This force of attraction is balanced by the centrifugal force.

$$\text{Centrifugal force} = \frac{mv^2}{r} \quad ...(ii)$$

Therefore, for balanced conditions, we can write;

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_o r^2}$$

$$mv^2 = \frac{Ze^2}{4\pi\epsilon_o r} \quad ...(iii)$$

Rearranging the above equation $\quad r = \frac{Ze^2}{4\pi\epsilon_o mv^2} \quad ...(iv)$

According to equation (iv), the radius of a moving electron is inversely proportional to the square of its velocity. It conveys the idea, **that electron should move faster nearer to the nucleus in an orbit of smaller radius.** It also tells, that if hydrogen atom has many possible orbits, then the promotion of electron to higher orbits makes it move with less velocity.

The determination of velocity of an electron is possible while moving in the orbit. In order to eliminate the factor of velocity from equation (iv), we use 4th Bohr postulate. According to Bohr, angular momentum of the electron is given by

$$mvr = \frac{nh}{2\pi}$$

$$v = \frac{nh}{2\pi mr}$$

Taking square $\quad v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}$

Putting the value of v^2 in equation (iv), we have

$$r = \frac{Ze^2\, 4\pi^2m^2r^2}{4\pi\epsilon_o\, m\, n^2h^2}$$

$$1 = \frac{Ze^2\, \pi m r}{\epsilon_o n^2h^2}$$

$$r = \frac{\epsilon_o n^2h^2}{\pi m Ze^2} \quad ...(v)$$

For hydrogen atom Z = 1 , so the equation for radius of H-atom is

$$r = \frac{\epsilon_o n^2h^2}{\pi me^2} = \left(\frac{\epsilon_o h^2}{\pi me^2}\right)n^2 \quad ...(vi)$$

According to the equation (vi), the radius of hydrogen atom is directly proportional to the square of number of orbit (n). So, higher orbits have more radii and vice versa. The collection of parameters $\left(\frac{\epsilon_o h^2}{\pi m e^2}\right)$ in equation (vi) is a constant factor.

$$\frac{\epsilon_o h^2}{\pi m e^2} = 0.529\,\mathring{A} = 0.529\times10^{-10}\,m$$

Putting the value of $\frac{\epsilon_o h^2}{\pi m e^2}$ in equation (vi), we get

$$r = 0.529\,\mathring{A} \times n^2 \quad ...(vii)$$

Conclusion

(i) Putting the value of n as 1, 2, 3, 4,...... the radius of orbits of hydrogen atoms are

$n = 1$ $\quad r_1 = 0.529\,\mathring{A}$

$n = 2$ $\quad r_2 = 0.529 \times (2)^2 = 2.11\,\mathring{A}$

$n = 3$ $\quad r_3 = 0.529 \times (3)^2 = 4.75\,\mathring{A}$

$n = 4$ $\quad r_4 = 0.529 \times (4)^2 = 8.4\,\mathring{A}$

$n = 5$ $\quad r_5 = 0.529 \times (5)^2 = 13.22\,\mathring{A}$

(ii) The comparison of radii shows that the distance between orbits of hydrogen atom goes on increasing as we move from 1st orbit to higher orbits. The orbits are not equally spaced.

$$r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < ......$$

(iii) Second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and similarly the 4^{th} orbit is sixteen times away.

Q.8 Derive the formula for calculating the energy of an electron in n^{th} orbit using Bohr's model.

Energy of Revolving Electron

The total energy of an electron in an orbit is equal to the sum of kinetic energy and potential energy.

$$E = E_{Kinetic} + E_{Potential}$$

$$K.E. = \frac{1}{2}mv^2$$

The value of potential energy can be calculated as follows:

The electrostatic force of attraction between the nucleus and the electron is given by $\frac{Ze^2}{4\pi\epsilon_o r^2}$.

If electron moves through a small distance dr, then the work done for moving electron is given by

Work done $=$ Force $\times$ distance

$$\text{Work done} = \frac{Ze^2}{4\pi\epsilon_o r^2}\times dr$$

In order to calculate the potential energy of the electron at a distance r from the nucleus, we calculate the total work done for bringing electron from infinity to a point at a distance r from the nucleus. This can be obtained by integrating the above expression between the limits of infinity and r.

$$\int_\infty^r \frac{Ze^2}{4\pi\epsilon_o r^2}dr = \frac{Ze^2}{4\pi\epsilon_o}\int_\infty^r \frac{1}{r^2}dr = \frac{Ze^2}{4\pi\epsilon_o}\left|-\frac{1}{r}\right|_\infty^r = \frac{Ze^2}{4\pi\epsilon_o}\left(-\frac{1}{r}\right) = -\frac{Ze^2}{4\pi\epsilon_o r}$$

The work done is the potential energy of electron, so

$$\text{Work done} = E_{potential} = -\frac{Ze^2}{4\pi\epsilon_o r} \quad ...(i)$$

The minus sign indicates that the potential energy of electron decreases, when it is brought from infinity to a point at a distance r from the nucleus. At infinity, the electron is not being attracted by any thing and the potential energy of the system is zero. Whereas at a point nearer the nucleus, it will be attracted by the nucleus and the potential energy becomes less than zero. The quantity less than zero is negative. For this reason potential energy given by equation (i) is negative

The total energy of electron is

$$E = E_{Kinetic} + E_{Potential}$$

$$E = \frac{1}{2}mv^2 + \left(-\frac{Ze^2}{4\pi\epsilon_o r}\right)$$

$$E = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\epsilon_o r} \quad ...(ii)$$

To eliminate the factor of velocity from equation (ii), putting the value of mv^2 from following equation

$$mv^2 = \frac{Ze^2}{4\pi\epsilon_o r}$$

$$E = \frac{Ze^2}{8\pi\epsilon_o r} - \frac{Ze^2}{4\pi\epsilon_o r}$$

$$E = \frac{Ze^2 - 2Ze^2}{8\pi\epsilon_o r}$$

Simplifying it, $$E = -\frac{Ze^2}{8\pi\epsilon_o r} \quad ...(iii)$$

Since $$r = \frac{\epsilon_o n^2 h^2}{\pi m Z e^2}$$

Putting the value of r from above equation in eq. (iii), we get

$$E_n = -\frac{Z^2 e^4 m}{8\epsilon_o^2 n^2 h^2} \quad ...(iv)$$

where E_n is the energy of nth orbit

For hydrogen atom, the number of protons in nucleus is one, so (Z = 1).

$$E_n = -\frac{e^4 m}{8\epsilon_o^2 n^2 h^2}$$

$$E_n = -\frac{e^4 m}{8\epsilon_o^2 h^2}\left[\frac{1}{n^2}\right] \quad ...(v)$$

Eq. (v) gives the energy of electron revolving around the nucleus of hydrogen atom.

The factors outside bracket are all constants. Putting the values of these constants, we get

$$\frac{e^4 m}{8\epsilon_o^2 h^2} = 2.178\times10^{-18}\,J$$

The equation (v) can be written as,

$$E_n = -2.178\times10^{-18}\left[\frac{1}{n^2}\right]J \quad ...(vi)$$

This equation gives the energy associated with electron in the nth orbit of hydrogen atom. Its negative value shows that electron is bound by the nucleus i.e. electron is under the force of attraction of the nucleus. Actually, the electron has been brought from infinity to distance r from the nucleus.

The value of energy obtained for the electron is in Joules/atom. If, this quantity is multiplied by Avogadro's number and then divided by 1000, the value of E_n will become

$$E_n = -\frac{2.178\times10^{-18}}{1000}\times6.02\times10^{23}\left[\frac{1}{n^2}\right]\text{kJmol}^{-1}$$

$$E_n = -\frac{1313.315}{n^2}\text{kJmol}^{-1} \qquad ...(vii)$$

As one mole of H = 1.008 g. So $\frac{1313.31}{n^2}\text{kJmol}^{-1}$ is the energy associated with 1.008 g of H. i.e. with Avogadro's number of atoms of hydrogen.

Substituting the value of n as 1, 2, 3, 4, 5, etc. in equation (vii), we get the energy associated with an electron revolving in 1st, 2nd, 3rd, 4th and 5th orbit of H-atom

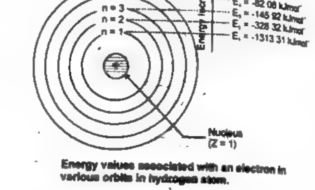
$$E_1 = -\frac{1313.315}{(1)^2} = -1313.315 \text{ kJ mol}^{-1}$$

$$E_2 = -\frac{1313.315}{(2)^2} = -328.32 \text{ kJ mol}^{-1}$$

$$E_3 = -\frac{1313.315}{(3)^2} = -145.92 \text{ kJ mol}^{-1}$$

$$E_4 = -\frac{1313.315}{(4)^2} = -82.08 \text{ kJ mol}^{-1}$$

$$E_5 = -\frac{1313.315}{(5)^2} = -52.53 \text{ kJ mol}^{-1}$$



Energy values associated with an electron in various orbits in hydrogen atom.

The values of energy differences between adjacent orbits can be calculated as follows:

$$E_2 - E_1 = (-328.32) - (-1313.31)$$
$$= -328.32 + 1313.31 = 984.99 \text{ kJ/mol}$$
$$E_3 - E_2 = (-145.92) - (-328.32)$$
$$= -145.92 + 328.32 = 182.40 \text{ kJ/mol}$$
$$E_4 - E_3 = (-82.08) - (-145.92)$$
$$= -82.08 + 145.92 = 63.84 \text{ kJ/mol}$$

The differences in the values of energy go on decreasing from lower to higher orbits.

$$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > ......$$

The energy difference between first and infinite levels of energy is calculated as:

$$E_\infty - E_1 = 0 - (-1313.315) = 1313.315 \text{ kJ mol}^{-1}$$

It shows that 1313.315 kJ mol⁻¹ is the ionization energy of hydrogen. This value is the same as determined experimentally.

Caution

The above values show that the energy differences between adjacent orbits of Bohr's model of hydrogen atom go on decreasing sharply. Keep in mind, that **distances between adjacent orbits increase.**

Q7a. Which postulate of Bohr's atomic model tells us that orbits are stationary and energy is quantized?

Ans. 1st postulate of Bohr's model:

"Electron revolves around the nucleus in one of the circular orbits. Each orbit has a fixed energy and a quantum number is assigned to it."

So, 1st postulate tells us that an orbit is stationary. By putting the value of n = 1, 2, 3, ---- in Bohr's equation for radius and energy, one can find the radius and energy corresponding to that orbit in which an electron is revolving. In other words, we can say that orbits are quantized.

Q7c. How does Bohr's equation tell you that?

(i) Radius is directly proportional to the square of the number of orbit.

Ans. According to Bohr's equation

$$r_n = \frac{\epsilon_o n^2 h^2}{\pi m Z e^2}$$

Where ϵ_o, h^2, π, m, e are constant values.

By putting the values of these constants and solving Bohr's equation we obtain

$$r_n = 0.529\frac{n^2}{Z}\overset{\circ}{A}$$

This equation simply relates radius of an orbit with its principle quantum number as

$$r_n \propto n^2$$

So, we can say that radius is directly proportional to the square of number of orbit (n)

Q7c. (ii) How does Bohr's equation tell that radius is inversely proportional to the number of protons in the nucleus?

Ans. According to Bohr's equation:

$$r_n = \frac{\epsilon_o n^2 h^2}{\pi m Z e^2}$$

where ϵ_o, h^2, π, m, e are constants.

By putting their values in equation, we get

$$r_n = 0.529\frac{n^2}{Z}\overset{\circ}{A}$$

$$r_n \propto \frac{1}{Z}$$

[Z is the number of proton in nucleus]

We can conclude from the above relation that greater the number of protons (Z) in nucleus, smaller will be the radius and vice versa.

Q7d. How do you come to know that the velocities of electrons in higher orbits are less than those in lower orbits of Hydrogen atom?

Ans. According to Bohr's equation, a moving electron in an orbit faces two equal but opposite forces i.e., a centripetal force and a centrifugal force.

$$\frac{Ze^2}{4\pi\epsilon_o r^2} = \frac{mv^2}{r}$$

$$\frac{1}{r} = \frac{4\pi\epsilon_o mv^2}{Ze^2}$$

$$\text{so} \quad r = \frac{Ze^2}{4\pi\epsilon_o mv^2}$$

Here Z, e, π, ϵ_o, m are constants for hydrogen, so

$$r \propto \frac{1}{v^2}$$

This equation shows that the velocities of electron in high orbits are less than those in the lower orbits of hydrogen atom and vice versa.

Q7a. Justify that the distance gaps between orbits go on increasing from lower to higher orbits.

Ans. Bohr's equation for radius $r_n = \frac{\epsilon_o n^2 h^2}{\pi m Z e^2}$

After solving the values of constants

Bohr's equation for $r_n = 0.529 \frac{n^2}{Z}$ Å

To prove the asked statement, we can apply this equation on Hydrogen atom.

Z for hydrogen = 1

n = 1, 2, 3, ...

$r_n = r_1, r_2, r_3, r_4, ...$

for n = 1 , r_1 = 0.529 Å
n = 2 , r_2 = 2.11 Å
n = 3 , r_3 = 4.75 Å
n = 4 , r_4 = 8.4 Å
n = 5 , r_5 = 13.22 Å

Now, we can calculate the distance gaps between two orbits i.e.,

$r_2 - r_1$ = 2.11 Å − 0.529 Å = 1.58 Å
$r_3 - r_2$ = 4.75 Å − 2.11 Å = 2.64 Å
$r_4 - r_3$ = 8.4 Å − 4.75 Å = 3.65 Å
$r_5 - r_4$ = 13.22 Å − 8.4 Å = 4.82 Å

We can say that distance gaps between orbits go on increasing from lower to higher orbits.

$$(r_2 - r_1) < (r_3 - r_2) < (r_4 - r_3) < (r_5 - r_4)$$

Q8a. Why potential energy of bounded electron is negative?

Ans. At infinity, the electron is not being attracted by anything and the potential energy of system is zero. Whereas at a point nearer to nucleus, it will be attracted by nucleus and potential energy of system becomes less than zero. (Attractive forces decrease the P.E.)

The quantity less than zero is –ive therefore P.E. of electron is negative when it is brought from infinity to a point at a distance 'r' from nucleus.

Q8b. Total energy of bounded electron is negative.

Ans. We know that total energy of a system is sum of its potential energy and kinetic energy.

$$E = K.E. + P.E.$$

By solving the K.E. + P.E. for electron the values, we get

$$E_n = \left(\frac{Ze^2}{8\pi\epsilon_o r}\right) + \left(-\frac{Ze^2}{4\pi\epsilon_o r}\right)$$

as value of P.E. is greater so its negative sign is used with total energy by subtraction

$$E_n = -\frac{Ze^2}{8\pi\epsilon_o r}$$

So, E_n has a –ive sign.

Q8c. Energy of an electron is inversely proportional to n^2 but energies of higher orbits are always greater than those of the lower orbits.

Ans. According to Bohr's equation for energy of electron

$$E_n = -\frac{mZ^2e^4}{8\epsilon_o^2 n^2 h^2}$$

For an atom values of m, Z, e, ϵ_o, h are constants. So

$$E \propto -\frac{1}{n^2}$$

From the above relationship, it is concluded that smaller the value of n, greater will be the value of E with –ive sign and vice versa.

Less negative values are actually larger while more negative values are smaller

For hydrogen Z = 1 the values of E_1, E_2 are as follows

for n = 1, E_1 = −1313.315 kJ mol^{-1}
n = 2, E_2 = −328.32 kJ mol^{-1}

− 328.32 kJ mol^{-1} (E_2) value is greater than −1313.315 kJ mol^{-1} (E_1).

Q8d. The Energy difference between two adjacent levels goes on decreasing sharply.

Ans. According to Bohr's equation E_n is

$$E_n = -1313.315\left[\frac{1}{n^2}\right] kJmol^{-1} \quad [Z \text{ for } H = 1]$$

Substituting the value of n = 1, 2, 3, 4, ... we can calculate

E_1 = −1313.315 kJ mol^{-1}
E_2 = −328.32 kJ mol^{-1}
E_3 = −145.92 kJ mol^{-1}
E_4 = −82.08 kJ mol^{-1}

Values of energy difference between two adjacent orbits can be calculated as

$E_2 - E_1$ = (−328.32) − (−1313.315) = 984.99 kJ mol^{-1}
$E_3 - E_2$ = (−145.92) − (−328.32) = 182.40 kJ mol^{-1}
$E_4 - E_3$ = (−82.08) − (−1459.2) = 63.84 kJ mol^{-1}

We conclude that energy difference between two levels goes on decreasing from lower to higher orbits

$$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > ....$$

Q9a. (i) Give an expression for energy difference between two levels, n_1 and n_2 for hydrogen atom.

Ans. According to Bohr's equation

$$E_n = -\frac{mZ^2e^4}{8\epsilon_o^2 h^2 n^2}$$

We can deduce the values of E_1 and E_2 for n_1 and n_2 as follows:

Z for Hydrogen = 1

for n = 1 , $E_1 = -\frac{me^4}{8\epsilon_o^2 h^2 n_1^2}$

$n = 2$, $E_2 = -\frac{me^4}{8\epsilon_o^2 h^2 n_2^2}$

$$\Delta E = E_2 - E_1$$

$\therefore$ We can say that

$$\Delta E = \left(\frac{-me^4}{8\epsilon_o^2 h^2 n_2^2}\right) - \left(\frac{-me^4}{8\epsilon_o^2 h^2 n_1^2}\right)$$

$$\Delta E = \frac{me^4}{8\epsilon_o^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Q9a. (ii) How expression for ΔE from Bohr's equation can be used to calculate the frequency of emitted or absorbed photon.

Ans. According to Bohr's equation

$\Delta E = h\upsilon$ .....(i)

The energy difference between two levels n_1 and n_2 is

$$\Delta E = \frac{Z^2 me^4}{8\epsilon_o^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

But $Z = 1$ (for Hydrogen atom)

$$\Delta E = \frac{me^4}{8\epsilon_o^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \quad \text{.....(ii)}$$

We can substitute the value of ΔE from eq. (i) in eq. (ii)

$$h\upsilon = \frac{me^4}{8\epsilon_o^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\therefore \upsilon = \frac{me^4}{8\epsilon_o^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

So this equation shows that the frequency of the photons when electron jumps from n_1 to n_2 orbits.

Q9a. (iii) How wave number of the photon is calculated from Bohr's equation?

Ans. According to Bohr's equation for frequency of a photon

$$\upsilon = \frac{me^4}{8\epsilon_o^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad [\because \upsilon = c\bar{\upsilon}]$$

$$c\bar{\upsilon} = \frac{me^4}{8\epsilon_o^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\therefore \bar{\upsilon} = \frac{me^4}{8\epsilon_o^2 h^3 c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

After calculating the constants of the equation we obtain

$$\bar{\upsilon} = 1.09678 \times 10^7\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] m^{-1}$$

So wave number of photon can also be calculated.

Q11a. Hydrogen atom and He^+ are mono electronic system but the size of He^+ is much smaller than H why?

Ans. Although both H atom and He^+ are mono electronic system means containing one electron, yet size of He^+ is smaller than H because

Number of protons in He^+ nucleus = 2

Number of protons in H nucleus = 1

Force of attraction between two protons of He^+ for one electron is greater than force of attraction between one proton and one electron in H-atom. Therefore, size of He^+ is smaller than H-atom.

We can prove this by Bohr's equation as well.

$$r_n = 0.529\frac{n^2}{Z}\,\mathring{A}$$

radius of first orbit for both atoms is

$$r_H = 0.529 \times \frac{1^2}{1} = 0.529\,\mathring{A}$$

$$r_{He^+} = 0.529 \times \frac{1^2}{2} = 0.2645\,\mathring{A}$$

so $r_{He^+} < r_H$ is proved.

Q11b. Do you think the size of Li^{+2} is even smaller than He^+. Justify with calculations.

Ans. Yes size of Li^{+2} is much smaller than He^+ because of difference in forces of attraction between nuclei and electrons for both atoms.

Number of protons in Li^{+2} = 3

Number of protons in He^{+1} = 2

Li^{+3} nucleus holds the electron tightly so its radius is smaller than He^+.

It can be proved mathematically

$$r_n = 0.529\frac{n^2}{Z}\,\mathring{A} \qquad \text{(Bohr's equation for radius)}$$

$$r_{He^+} = 0.529 \times \frac{1^2}{2} = 0.2645\,\mathring{A} \qquad (Z = 2 \text{ for } He^{+1})$$

$$r_{Li^{+2}} = 0.529 \times \frac{1^2}{3} = 0.176\,\mathring{A} \qquad (Z = 3 \text{ for } Li^{+2})$$

So $r_{He^{+1}} > r_{Li^{+2}}$

SPECTRUM

"A visual display or dispersion of components of white light when it is passed through a prism is called spectrum."

The study of spectrum is called **spectroscopy**. The instrument used to analyze spectrum is called **spectrometer**

Explanation

When a radiation of light is passed through a prism, the rad[illegible] undergoes refraction or bending. The extent of bending depends upon the wavelength of the photons. A radiation [illegible] wavelength is bent to a smaller degree than the radiation of a shorter wavelength. Ordinary white light consists of [illegible]ations of all wavelengths. After passing through the prism, white light is splitted up into radiations of different wavelen[illegible].

The colours of visible spectrum are violet, indigo, blue, gr[illegible] yellow, orange and red and their wavelengths range from 400 nm to 750 nm. These radiations are called visible lig[illegible]ations because our eyes can detect only these radiations:

S. No.	Name	Source
1.	Radi[illegible] wave	Alternatin[illegible] current of high frequency
2.	Micro wave	[illegible]lystron tube
3.	Infrared (IR	In[illegible]descent objects
4.	Visible	[illegible] bulbs, sun rays
5.	Ultraviolet (UV)	Sun rays, a[illegible] lamps with mercury vapours
6.	X-Rays	Cathode rays striking metal plate

7.	γ-Rays	Secondary effect of radioactive decay
8.	Cosmic rays	Outer space

In addition to visible region of the spectrum, there are seven other regions. Ultra-violet X-rays, γ-rays and cosmic rays are towards the lower wavelength end of the spectrum and they possess the photons with greater energies. On the other side of the visible region, there lies infrared, microwaves and radio frequency regions. The arrangement of all types of electromagnetic radiations in the decreasing order of their wavelengths or increasing order of their frequencies is called electromagnetic spectrum

Spectrum is of two types

1 Continuous Spectrum   2 Line Spectrum

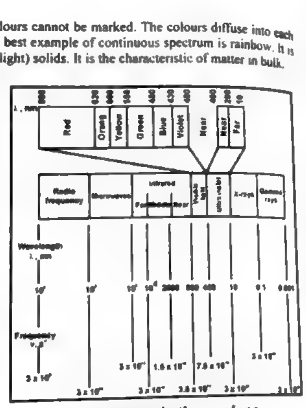
(1) Continuous spectrum

In this type of spectrum, the boundary line between the colours cannot be marked. The colours diffuse into each other. One colour merges into another without any dark space. The best example of continuous spectrum is rainbow. It is obtained from the light emitted by the sun or incandescent (electric light) solids. It is the characteristic of matter in bulk.

(2) Line spectrum (atomic spectrum)

When an element or its compound is volatilized on a flame and the light emitted is seen through a spectrometer, we see distinct lines separated by dark spaces. This type of spectrum is called line spectrum or atomic spectrum. This is characteristic of an atom. Each element has its own line spectrum. The number of lines and the distance between them depend upon the element volatilized.

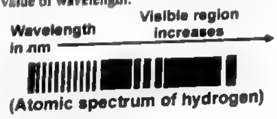
Atomic spectrum can also be observed when elements in gaseous state are heated at high temperature or subjected to an electric discharge.



The visible and other regions of spectrum

Examples

- Line spectrum of sodium contains two yellow coloured lines separated by a definite distance.
- The spectrum of hydrogen consists of a number of lines of different colours having different distances between them. It has also been observed that distances between the lines for the hydrogen spectrum decrease with the decrease in wavelength and the spectrum becomes continuous after a certain value of wavelength.



(Atomic spectrum of hydrogen)

Types of Atomic Spectrum

There are two ways in which an atomic spectrum can be viewed.

(i) Atomic emission spectrum

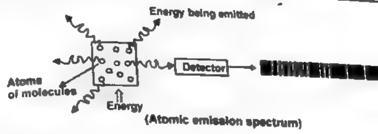
(ii) Atomic absorption spectrum

Atomic Emission Spectrum

When solids are volatilized or elements in their gaseous states are heated to high temperature or subjected to an electrical discharge, radiations of certain wavelengths are emitted. The spectrum of this radiation contained **bright lines against a dark background.** This is called atomic emission spectrum.

(i) Each element has its characteristic spectrum just as each individual has its characteristic finger print.

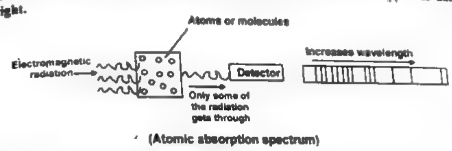
(ii) Each line in the spectrum corresponds to a particular wavelength or frequency.



(Atomic emission spectrum)

Atomic Absorption Spectrum

When a beam of white light is passed through a gaseous sample of an element, the element absorbs certain wavelengths while the rest of wavelengths pass through it. The spectrum of this radiation is called an atomic absorption spectrum. The wavelengths of the radiation that have been absorbed by the element appear as **dark lines and the background is bright.**



(Atomic absorption spectrum)

Similarities of emission and absorption spectra

It is interesting to note that the wavelengths of the dark line in the absorption spectrum of a substance are the same as those of the wavelengths of the bright lines in the emission spectrum of the same substance

In emission spectrum these lines appear bright because the corresponding wavelengths are being emitted by the element whereas they appear dark in the atomic absorption spectrum because the wavelengths are being absorbed by the element

Q108. What is spectrum? Differentiate between continuous spectrum and line spectrum.

Ans. "A visual display or dispersion of components of white light, when it is passed through a prism is called spectrum."

Comparison of continuous and line spectra

Continuous spectrum	Line spectrum
1. In this spectrum, the boundary line between the colours cannot be marked.	1. In this spectrum, we see distinct coloured lines
2. One colour merge into other without any dark space.	2. Distinct coloured lines are separated by dark spaces.
3 It is a characteristic of matter in bulk	3. It is the characteristic of atom
4. Examples. Rainbow, white light of sun and light from an incandescent source.	4. Examples. (i) Spectrum obtained from H_2 (ii) Na-spectrum

Q109. Compare line emission and line absorption spectra.

Ans.

Differences between emission and absorption spectra

Line emission spectrum	Line absorption spectrum
1. It is spectrum formed by elements or their compounds when they are heated in flame or subjected to electric discharge	1. When beam of white light is passed through vapours of element, it absorbs certain wavelengths, rest of wavelength pass thrown it

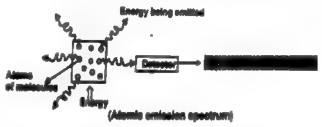
2 Sample is in gaseous and excited state.	2. Sample is in gaseous, liquid or solid state.
3. Spectrum of this radiation consists of bright lines against a dark background.	3. Here spectrum appears in the form of dark lines on bright background.

(b) Similarities of emission and absorption spectra:

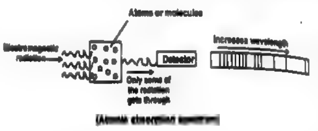
(i) Absorption spectrum is the photographic negative of emission spectrum.

(ii) The dark lines in absorption spectrum appears exactly at the same position where the bright lines appear in emission spectrum for a same sample.

(iii) Both spectra are actually the finger prints of atoms of various elements and help in identification of elements.



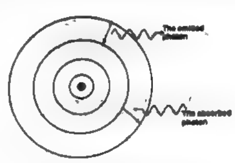
(Atomic emission spectrum)



(Atomic absorption spectrum)

Q10c. What is the origin of line spectrum?

Ans. According to Bohr's atomic model, the energy of an electron remains constant in an orbit. If it jumps to higher orbit, it absorbs energy and during de-excitation it emits energy. Absorbed energy is in the form of dark lines obtained in absorption spectrum while emitted energy is in the form of bright lines of emission spectrum. In this way line spectrum is formed.



The electron emits or absorbed the energy during changing the orbits

Hydrogen Spectrum

Hydrogen-spectrum is an important example of atomic spectrum. Hydrogen is filled in a discharge tube. At a very low pressure a bluish light is emitted from the discharge tube. This light when viewed through a spectrometer shows several isolated sharp lines.

These are called spectral lines. The wavelengths of these lines lie in the visible, ultraviolet and infrared regions. These spectral lines can be classified into five groups called spectral series. These series are named after their discoverers as shown below:

(i) Lyman series (U.V region) (ii) Balmer series (visible region)
(iii) Paschen series (I.R region) (iv) Brackett series (I.R region)
(v) Pfund series (I.R region)

The first four series were discovered before Bohr's atomic model (1913). The wave numbers (m^{-1}) of the series of lines in hydrogen spectrum are given in the table below.

It is seen from the table that as we proceed from Lyman series to Pfund series, the wave numbers (m^{-1}) of spectral lines decrease. The lines of Balmer series have been given specific names as H_α, H_β, …… etc.

Wave numbers (m^{-1}) of various series of hydrogen spectrum

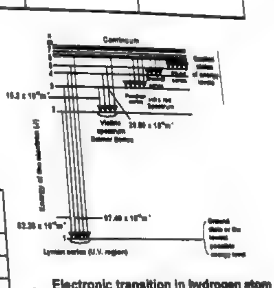
Lyman series (U.V region)	Balmer series (Visible region)	Paschen series (I.R region)	Brackett series (I.R region)	Pfund series (I.R region)
82.20×10^5 97.60×10^5 102.70×10^5 105.20×10^5 106.20×10^5 107.10×10^5	15.21×10^5 (H_α line) 20.60×10^5 (H_β line) 23.5×10^5 (H_γ line) 24.35×10^5 (H_δ line) 25.18×10^5	5.30×10^5 7.80×10^5 9.12×10^5 9.95×10^5	2.46×10^5 3.80×10^5 4.61×10^5	1.34×10^5 2.14×10^5

Origin of Hydrogen Spectrum on the Basis of Bohr's Model

According to Bohr, electron in hydrogen atom may revolve in any orbit depending upon its energy. When hydrogen gas is heated or subjected to an electric discharge, its electron moves from one of the lower orbit to higher orbit, absorbing particular wavelength of energy.

Subsequently, when it comes back, the same energy is released. This energy is observed as radiation of particular wavelengths in the form of bright lines seen in the certain region of the emission spectrum of hydrogen gas.

Spectral series	Lower orbit (n_1)	Higher orbit (n_2)	Appearing in
Lyman series	1	2, 3, 4, 5,…	U.V. region
Balmer series	2	3, 4, 5,….	Visible region
Paschen series	3	4, 5, 6,…..	Infrared region
Brackett series	4	5, 6,……	Infrared region
Pfund series	5	6, 7,…	Infrared region



Electronic transition in hydrogen atom and series of spectral lines, justified by Bohr's model of atom

Calculations of Wave Numbers of Photon of Various Spectral Series by Bohr's Theory

The wavelength (λ) or wave number ($\bar{\upsilon}$) of a spectral line depends on the quantity of energy emitted by the electron. Suppose an electron jumps from a high energy orbit n_2 to a low energy orbit n_1 and emits a photon of light. According to Bohr's equation:

Energy of electron in n_1 orbit is:

$$E_1 = -\frac{Z^2e^4m}{8\epsilon_0^2 n_1^2h^2}$$

Energy of electron in n_2 orbit is:

$$E_2 = -\frac{Z^2e^4m}{8\epsilon_0^2 n_2^2h^2}$$

The difference of energy between the two orbits is

$$\Delta E = E_2 - E_1$$

$$\Delta E = \left[-\frac{Z^2e^4m}{8\epsilon_0^2 n_2^2h^2}\right] - \left[-\frac{Z^2e^4m}{8\epsilon_0^2 n_1^2h^2}\right]$$

$$\Delta E = -\frac{Z^2e^4m}{8\epsilon_0^2 n_2^2h^2} + \frac{Z^2e^4m}{8\epsilon_0^2 n_1^2h^2}$$

$$\Delta E = \frac{Z^2e^4m}{8\epsilon_o^2 h^2}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] \quad ...(i)$$

For H atom $Z = 1$ and $\frac{e^4m}{8\epsilon_o^2 h^2} = 2.18\times10^{-18}$ J (By putting the values of constants)

Putting these values in the above equation, we get

$$\Delta E = 2.18\times10^{-18}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]\text{Joule} \quad ...(ii)$$

With the help of equation (ii), the energy difference between any two orbits of H-atom can be calculated where n_1 is the lower level and n_2 is higher level. It is not necessary that n_1 and n_2 are adjacent orbits.

Frequency

Since $\Delta E = h\upsilon$

Therefore, equation (i) becomes

$$h\upsilon = \frac{Z^2e^4m}{8\epsilon_o^2 h^2}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$\upsilon = \frac{Z^2e^4m}{8\epsilon_o^2 h^3}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] \quad ...(iii)$$

For H-atom $Z = 1$

$$\upsilon = \frac{e^4m}{8\epsilon_o^2 h^3}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]\text{Hz} \quad ...(iv)$$

Frequency has the **units of cycles s^{-1} or Hertz (Hz) (1Hz = cycle s^{-1})**

This equation gives us the frequency of a photon emitted when electron jumps from higher orbit to a lower orbit in the H-atom. The frequency values go on decreasing between adjacent levels.

Wave Number

Since $\upsilon = c\,\bar{\upsilon}$

Therefore, equation (iii) becomes

$$c\,\bar{\upsilon} = \frac{Z^2e^4m}{8\epsilon_o^2 h^3}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$\bar{\upsilon} = \frac{Z^2e^4m}{8\epsilon_o^2 h^3c}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

For H-atom $Z = 1$

$$\bar{\upsilon} = \frac{e^4m}{8\epsilon_o^2 h^3c}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] \quad ...(v)$$

All the terms in $\frac{e^4m}{8\epsilon_o^2 h^3c}$ are constant and have been calculated to be $1.09678 \times 10^7\ m^{-1}$. This is called **Rydberg constant**

So, equation (v) becomes

$$\bar{\upsilon} = 1.09678\times10^7\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]m^{-1} \quad .....(vi)$$

Equation (vi) gives the values of wave number of photons emitted or absorbed when the electron jumps between n_1 and n_2 orbits

Let us calculate the **wave number of lines of various series**

Lyman Series

First line

$n_1 = 1$(lower orbit) $\qquad n_2 = 2$ (higher orbit)

$$\bar{\upsilon} = 1.09678\times10^7\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] = 82.26\times10^5\ m^{-1}$$

Second line

$n_1 = 1 \qquad n_2 = 3$

$$\bar{\upsilon} = 1.09678\times10^7\left[\frac{1}{(1)^2}-\frac{1}{(3)^2}\right] = 97.49\times10^5\ m^{-1}$$

Limiting line

$n_1 = 1 \qquad n_2 = \infty$

$$\bar{\upsilon} = 1.09678\times10^7\left[\frac{1}{(1)^2}-\frac{1}{(\infty)^2}\right] = 109.678\times10^5\ m^{-1}$$

Limiting line is developed, when electron jumps from infinite orbit to, n = 1

The values of all these wave numbers lie in the U.V. region of the spectrum. It means that when electron of H-atom falls from all the possible higher levels to $n_1 = 1$ then the photon of radiation lie in the range of U.V. region

Balmer Series

First line

$n_1 = 2$ (lower orbit) $\qquad n_2 = 3$ (higher orbit)

$$\bar{\upsilon} = 1.09678\times10^7\left[\frac{1}{(2)^2}-\frac{1}{(3)^2}\right] = 15.234\times10^5\ m^{-1}$$

Second line

$n_1 = 2 \qquad n_2 = 4$

$$\bar{\upsilon} = 1.09678\times10^7\left[\frac{1}{(2)^2}-\frac{1}{(4)^2}\right] = 20.566\times10^5\ m^{-1}$$

Third line

$n_1 = 2 \qquad n_2 = 5$

$$\bar{\upsilon} = 1.09678\times10^7\left[\frac{1}{(2)^2}-\frac{1}{(5)^2}\right] = 23.00\times10^5\ m^{-1}$$

Limiting line

$n_1 = 2 \qquad n_2 = \infty$

$$\bar{\upsilon} = 1.09678\times10^7\left[\frac{1}{(2)^2}-\frac{1}{(\infty)^2}\right] = 27.421\times10^5\ m^{-1}$$

The limiting line of Balmer series lie in the U.V. region while all other lines fall in the visible region.

Similarly, we can calculate the wave numbers for all the lines of Paschen, Brackett and Pfund series. These three series of lines lie in the infrared region.

Defects of Bohr's Atomic Model

1. Spectrum of multi-electrons system

Bohr's theory can successfully explain the origin of the spectrum of H-atom and ions like He^{+1}, Li^{+2} and Be^{+3}, etc. These are all one electron systems. But this theory is not able to explain the origin of the spectrum of multi-electrons or poly-electrons systems like He, Li and Be, etc.

2. Fine structures or multiple structures

When the spectrum of hydrogen gas is observed by means of a high resolving power spectrometer, the individual spectral lines are replaced by several very fine lines, i.e. original lines are seen divided into other lines. The H_α-line in the Balmer series is found to consist of five component lines. This is called fine structure or multiple structure. Actually, the appearance of several lines in a single line suggests that only one quantum number is not sufficient to explain the origin of various spectral lines.

3. Three dimensional motion of electron

Bohr suggested circular orbits of electrons around the nucleus of hydrogen atom, but researches have shown that the motion of electron is not in a single plane, but takes place in three dimensional space. Actually, the atomic model is not flat.

4. Zeeman effect / stark effect

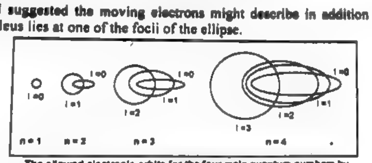
When the excited atoms of hydrogen (which give an emission line spectrum) are placed in a magnetic field, its spectral lines are further split up into closely spaced lines. This type of splitting of spectral lines is called **Zeeman effect.** So, if the source which is producing the Na-spectrum is placed in a weak magnetic field, it causes the splitting of two lines of Na into com[illegible]nt lines.

When the excited hydrogen atoms are placed in an electrical field, its spectral lines are further split up into closely spaced lines. This type of splitting of spectral lines is called **"Stark effect."**

Bohr's theory does not explain either Zeeman or Stark effect.

5. Sommerfeld's contribution

In 1915, Sommerfeld suggested the moving electrons might describe in addition to the circular orbits elliptic orbits as well wherein the nucleus lies at one of the focii of the ellipse.



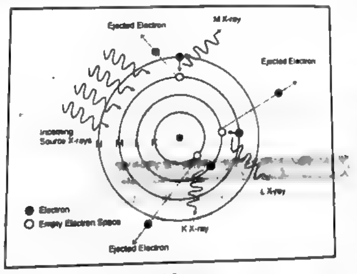
The allowed electronic orbits for the four main quantum numbers by the Bohr-Sommerfeld model.

X-RAYS

"Electromagnetic radiations of very short-wavelengths (0.1–20 Å) produced when rapidly moving electrons collide with heavy metal anode in the discharge tube are called X-rays."

Origin of X-rays

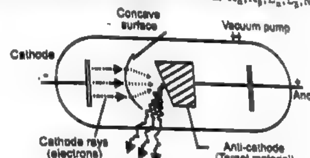
When the fast moving cathode rays (electrons) strike the target metal, they are able to remove electrons from the inner orbits or shells of the metal atoms. This will create a vacancy in the inner shells. Due to the influence of the stronger nuclear charge, the electrons will step down from a higher energy orbit to the lower energy orbit in order to fill that vacancy. This **inner shell transition of electrons** causes the emission of radiation in the form of X-rays.



Production of X-rays

X-rays are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube. Energy is released in the form of electromagnetic waves when the electrons are suddenly stopped. In the discharge tube, the electrons produced by a heated tungsten filament, are accelerated by high voltage. It gives them sufficient energy to bring about the emission of X-rays on striking the metal target. X-rays are emitted from the target in all directions, but only a small portion of them is used for useful purposes through the windows. The wavelength of X-rays produced depends upon the nature of the target metal. Every **metal has its own characteristic X-rays.**

The X-rays are passed through a slit in platinum plate and then emerged through aluminum window. This is thrown on a crystal of $K_4[Fe(CN)_6]$, which analyses the X-ray beam. The rays are diffracted from the crystal and are obtained in the form of line spectrum of X-rays. This is allowed to fall on photographic plate. This line spectrum is the characteristic of target material used. This characteristic X-rays spectrum has discrete spectral lines. These are grouped into K-series, L-series and M-series, etc. Each series has various lines as $K_\alpha, K_\beta, L_\alpha, L_\beta, M_\alpha, M_\beta$, etc



Production of X-rays

Conclusion drawn by Moseley from his research work

A systematic and comprehensive study of X-rays was undertaken by Moseley in 1913-1914. His researches covered a range of wavelengths 0.04-8 Å. He employed thirty eight different elements from aluminium (Al) to gold (Au), as target in X-rays tube.

(i) The spectral lines could be classified into two distinct groups.
- Spectral lines of shorter wavelengths are identified as K-series.
- Spectral lines of comparatively longer wavelengths are identified as L-series

(ii) If the target element is of higher atomic number the wavelength of X-rays becomes shorter

(iii) A very simple relationship was found between the frequency (υ) of a particular line of X-rays and the atomic number Z of the element emitting it.

$$\sqrt{\upsilon} = a(Z-b)$$

Here 'a' and 'b' are the constants characteristic of the metal under consideration. This linear equation is known as Moseley's Law. "a" is proportionality constant and "b" is called screening constant of the metals

Moseley's Law

"The frequency of a spectral line in the X-rays spectrum varies as the square of atomic number of an element emitting it."

Mathematically, it can be written as

$$\sqrt{\upsilon} = a(Z-b)$$

Where
- υ = frequency of spectral line
- Z = atomic number of target metal
- a = proportionality constant
- b = screening constant

This law convinces us that characteristic properties of the element (both physical and chemical) are determined by the atomic number and not by the atomic mass. If value of $\sqrt{\upsilon}$ for K-series are plotted against Z, then a straight line is obtained.

Importance of Moseley's Law in Chemistry

(i) Moseley arranged K and Ar, Ni and Co in a proper way in Mendeleev's periodic table

(ii) This law has led to the discovery of many new elements like Tc(43), Pr(59), Rh(45)

(iii) The atomic number of rare earths have been determined by this law.

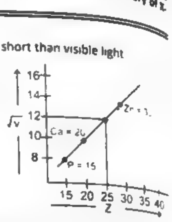
Q12a. What are X-rays? What is their origin? How was the idea of atomic number derived from the discovery of X-rays?

Ans. X-Rays:

X-rays are the electro-magnetic radiations with high frequency and wavelength short than visible light

Origin of X-rays

When cathode rays are converged on a metal target (taken as anode), then highly penetrating radiations are produced called X-rays. Their frequency is greater and wavelength is shorter than visible light.



X-rays and Atomic Number (Z):

The frequency of X-rays depends upon the proton number (Z) of an element and is the characteristic of an element. It is given by Moseley's law as

$$\sqrt{\upsilon} \propto Z$$

When graph is plotted between $\sqrt{v}$ on y-axis and Z on x-axis, a straight line is obtained for different elements

Q12b. How does the Bohr's model justify the Moseley's equations?

Ans. Bohr's equation for frequency is:

$$\upsilon = \frac{Z^2e^4m}{8\varepsilon_0^2h^3}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

If we consider it for similar transition ($n_2 = 2$ to $n_1 = 1$) of electron for different elements.

Then we have a relation.

$$\upsilon \propto Z^2$$

$$\sqrt{\upsilon} \propto Z$$

or $$\sqrt{\upsilon} \propto Z-b$$

$$\sqrt{\upsilon} = a(Z-b) \text{ Moseley's equation}$$

$\frac{me^4}{8\varepsilon_0^2h^3}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$ is constant for similar transition of different elements. Since frequency is reduced by screening constant (b).

Wave-Particle Nature of Matter (Dual Nature of Matter)

Introduction

Planck's quantum theory of radiation tells us that light shows a dual character i.e., it behaves both as a material particle and as wave. This idea was extended to matter particles in 1924 by Louis de-Broglie.

Wave-particle duality

According to de-Broglie, all matter particles in motion have a dual character i.e. every material particle is also associated with wave like properties. It means that electrons, protons, neutrons, atoms and molecules possess the characteristics of material particles as well as of waves. This is called wave-particle duality in matter. He derived a mathematical equation which relates the wavelength (λ) of the electron to the momentum of electron.

$$\lambda = \frac{h}{mv}$$

This relationship is known as de-Broglie equation.

Here
λ = de-Broglie wavelength
h = Planck's constant
m = mass of the particle
v = velocity of the particle

According to this equation, the wavelength of the moving particle (electron) is inversely proportional to its momentum (mv).

Derivation of de-Broglie equation

According to Planck's equation

$$E = h\upsilon \quad \text{...(i)}$$

According to the Einstein's mass energy relation

$$E = mc^2 \quad \text{...(ii)}$$

Where 'm' is the mass of the material particle which has to convert itself into a photon, and 'c' is the velocity of photon. Equating two values of energy.

$$h\upsilon = mc^2 \quad \text{...(iii)}$$

Since $$\upsilon = \frac{c}{\lambda}$$

Putting the value of υ in equation (iii), we get

$$\frac{hc}{\lambda} = mc^2$$

or $$\lambda = \frac{h}{mc} \quad \text{...(iv)}$$

Considering that nature is symmetrical, we apply this equation (iv) to the moving electron of mass 'm' and velocity 'v'. This idea gives us the de-Broglie's equation as fellow,

$$\lambda = \frac{h}{mv}$$

This equation shows that the wavelength of electron is inversely proportional to momentum of electron

Applications of de-Broglie's Equation

(i) Electron

An electron moving with a velocity of 2.188×10^6 m/s in the first orbit of Bohr's model of hydrogen atom. The wavelength associated with it can be calculated as follow:

$$v = 2.188 \times 10^6 \text{ m/s}$$

$$h = 6.626 \times 10^{-34} \text{ Js} \qquad 1\text{ J} = 1\text{ kg m}^2\text{s}^{-2}$$

$$m = 9.108 \times 10^{-31} \text{ kg}$$

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{6.626\times10^{-34}\text{ Js}}{9.108\times10^{-31}\text{ kg}\times2.188\times10^{6}\text{ ms}^{-1}} = 0.33\times10^{-9}\text{ m}$$

$$\lambda = 0.33 \text{ nm}$$

This value of wavelength of electron while moving in the first orbit of hydrogen atom is comparable to the wavelength of X-rays and can be measured.

(ii) Proton

If we imagine a proton moving in a straight line with the same velocity as mentioned for electron, its wavelength will be 1836 times smaller than that of electron because proton is 1836 times heavier than electron.

(iii) α-particle

An α-particle moving with the velocity as that of electron should have a wavelength 4 times smaller than that of proton or 1836 × 4 = 7344 times smaller than that of electron.

(iv) Small stone

A stone of mass one gram (10^{-3} kg) moving with the velocity 10 m/s, its wavelength will be calculated as

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{6.626 \times 10^{-34}\,Js}{10^{-3}\,kg \times 10ms^{-1}}$$

$$\lambda = 6.626 \times 10^{-32}\,m$$

This wavelength is so small that it cannot be measured by any conceivable method.

Caution

It means that heavy material particles have waves associated with them, but they cannot be captured and we say **that the macroscopic bodies don't have the waves.**

Experimental verification of dual nature of matter

In 1927, two American scientists, Davisson and Germer did an experiment to verify the wave nature of moving electron. Electrons were produced from heated tungsten filament and accelerated by applying the potential difference through charged plates. Davisson and Germer proved that the accelerated electrons undergo diffraction, like waves, when they fall on a nickel crystal. In this way, the wave nature of electron got verified. Davisson and Germer got the noble prize for inventing an apparatus to prove the matter waves and de-Broglie got the separate noble prize for giving the equation of matter wave

Heisenberg's Uncertainty Principle

According to Bohr's theory, an electron is a material particle and its position as well as momentum can be determined with great accuracy. But after the concept of de-Broglie's wave nature of electron, it has not been possible for us to measure simultaneously the exact position and velocity of electron.

Introduction

In 1927, Werner Heisenberg attempted to explain the position and momentum (or velocity) of a small particle such as electron. He put forward uncertainty principle.

Statement

According to this principle

"It is impossible to measure simultaneously both the exact position and momentum of a microscopic particle like electron with certainty."

Mathematical form

Suppose, that Δx is the uncertainty in the measurement of position and Δp is the uncertainty in the measurement of momentum of an electron, then

$$\Delta x \,.\, \Delta p \geq \frac{h}{4\pi}$$

This relationship is called uncertainty principle. This equation shows that if Δx is small then Δp will be large and vice versa. So, if one quantity is measured accurately then the other becomes less accurate. Hence, certainty in the determination of one quantity introduces uncertainty in the determination of the other quantity.

Limitation

The uncertainty principle is applicable only for microscopic particles like electrons, protons, neutrons etc. and has no significance for large particles i.e. macroscopic particles. It is because the product of uncertainty in position and momentum for large particles is so small that it can be ignored.

Explanation

Compton's effect can help us understand the uncertainty principle. Suppose, we wish to determine the position of electron. Visible light cannot help us, because the wavelength of visible light is millions time large as compared to the diameter of electron. For this purpose, we have to use X-rays which have very short wavelength as compared to that of visible light. When this photon of X-rays strikes an electron, the momentum of electron will change. In other words, uncertainty of momentum will appear due to change of velocity of electron. Smaller the wavelength of X-rays, greater will be the energy of the photon. Hence, the collision of X-rays with electron will bring about the greater uncertainty in momentum. So, an effort to determine the exact position of electron has rendered its momentum uncertain. When we use the photons of longer wavelength to avoid the change of momentum, the determination of the position of electron becomes impossible.

In the case of bigger particles (having considerable mass), the value of uncertainty product is negligible. If the position is known quite accurately, i.e. Δx is very small, Δv becomes large and vice-versa, Thus, uncertainty principle is important only in the case of smaller moving particles like electrons.

Q.14 (a) Briefly discuss the wave mechanical model of atom. How has it given the idea of orbital.

Wave Mechanical Model of Atom

The main points of wave-mechanical model are given below:

(1) Electrons have got a dual nature.
(2) Electronic wave is a standing circular wave around the nucleus. It is a three dimensional wave moving in the electric field of the positively charged nucleus.
(3) Both position and momentum of an electron cannot be determined simultaneously with certainty
(4) The three dimensional region in space around the nucleus where we have maximum probability (95%) of finding an electron is called orbital.
(5) The energy and angular momentum of an electron is quantized.
(6) Electrons having different energies are to live in different regions.

Concept of Orbital

Bohr's model of atom is contradicted by Heisenberg's uncertainty principle. In Bohr's atom, the electrons are moving with specific velocities in orbits of specified radii, and according to uncertainty principle, both these quantities cannot be measured experimentally. A theory involving quantities, which cannot be measured, does not follow the tradition of scientific work.

In order to solve this difficulty, **Schrodinger, Heisenberg and Dirac** worked out wave theories of the atom. The best known treatment is that of Schrodinger. He set up a wave equation for hydrogen atom. According to Schrodinger, although the position of an electron cannot be found exactly, the probability of finding an electron at a certain position at any time can be found. The solution of the wave equation gives probability of finding an electron present in a given small region of space. When the probability of finding the electron at a distance r from the nucleus is calculated for the hydrogen atom in the ground state, Fig (i) is obtained.

Probable electron density diagram for hydrogen atom.

The maximum probability of finding the radius is at a distance of 0.053 m. It is the same radius as calculated for the Bohr's first orbit. There is a possibility that the electron is either closer to the nucleus or outside the radius of 0.053 nm, where probability of finding electron decreases sharply.

Atomic orbital

"The volume of space in which there is 95% chance of finding an electron is called atomic orbital."

The term orbital should not be confused with the term orbit as used in the Bohr's theory, the orbital can be regarded as a spread of charge surrounding the nucleus. This is often called the "electron cloud."

Q14a. Compare orbit and orbitals.

Difference between Orbit and Orbital

Ans.

Orbit	Orbital
1. It is a definite path in which an electron moves around nucleus as proposed by Bohr.	1. It is three dimensional space around nucleus where the probability of finding electron is maximum (95%)
2. Orbits are circular in shape.	2. Orbitals have different shapes e.g. s-orbital is spherically symmetrical, p-orbitals are dumb bell shaped etc.
3. Orbits do not have a directional character.	3. All orbitals have directional characters except s-orbital.
4. In an orbit, exact position and momentum of an electron can be measured with certainty (violation against Heisenberg's uncertainty principle.)	4. In an orbital, exact position and momentum of an electron can not be measured with certainty (obeying Heisenberg's uncertainty principle)

Ans.

Orbit	Orbital
5. It represents planar motion of electrons	5. It represents three dimensional motion of electrons.
6. Maximum no. of electrons in an orbit is given by $2n^2$ i.e., in 1, 2, 3 orbit electrons are 2, 8, 18.	6. An orbital can have a maximum of 2 electrons.

(b) What are quantum numbers? Discuss their significance.

QUANTUM NUMBERS

"The sets of numerical values which give the acceptable solution to Schrodinger wave equation for hydrogen atom are called quantum numbers."

or

"The number or labels which completely describe an electron in an atom is called quantum number."

There are four quantum numbers which can describe the electron completely.

(i) Principal quantum number (n)
(ii) Azimuthal quantum number (ℓ)
(iii) Magnetic quantum number (m)
(iv) Spin quantum number (s)

(i) Principal Quantum Number(n)

The different energy levels in Bohr's atom are represented by 'n'. This is called principal quantum number by Schrodinger. Its value is non-zero, positive integers upto infinity.

$$n = 1, 2, 3, 4, \ldots\ldots$$

n	1	2	3	4
Shell	K	L	M	N

The value of 'n' represents the shell or energy level in which the electron revolves around the nucleus.

Applications

(i) Radius of orbit: When we study the Bohr's atomic model, we represent the energy level by 'n'. This value of 'n' gives the value of radius of orbit. $r = 0.529\ (n^2)\ \mathring{A}$

(ii) Size of on orbit: The value of 'n' in Schrodinger wave equation tells us the distance of electron from nucleus. Greater the value of 'n', greater will be the size of orbit.

(iii) Energy of the orbit: The energy formula of Bohr's model also involves 'n'

$$E = -2.18 \times 10^{-18}\left(\frac{1}{n^2}\right) J$$

Greater the value of 'n', greater value of energy of electron.

(iv) Number of electrons: The maximum number of electrons that can be accommodated in any shell is given by the formula $2n^2$.

$n = 1$ (K) $2(1)^2 = 2$
$n = 2$ (L) $2(2)^2 = 8$
$n = 3$ (M) $2(3)^2 = 18$
$n = 4$ (N) $2(4)^2 = 32$

(ii) Azimuthal Quantum Number (ℓ)

In the defects of Bohr's model that a spectrometer of high resolving power shows that an individual line in the spectrum is further divided into several very fine lines. This thing can be explained by saying that each shell is divided into subshells. So only principal quantum number (n) is not sufficient to explain line spectrum. There is another subsidiary quantum number called **Azimuthal quantum number** and is used to represent the subshells.

Value: Its value are $\ell = 0, 1, 2, 3, \ldots\ldots (n-1)$

Its value depends upon n. These values represent different subshells which are designated by small letters s, p, d and f which stand for sharp, principal, diffused and fundamental respectively. These are the spectral terms used to describe the series of lines observed in the atomic spectrum.

Shapes of subshells

A subshell may have different shapes depending upon the nature of 'ℓ'

$\ell = 0$ s-subshell spherical shape
$\ell = 1$ p-subshell dumb bell shape
$\ell = 2$ d-subshell complicated shape (sausage shape)

ℓ	0	1	2	3	4	5
notation						

Relationship between principal and azimuthal quantum number

The relationship between principal and Azimuthal quantum numbers is as follows.

n = 1	K-shell	$\ell = 0$	s-subshell	1s
n = 2	L-shell	$\ell = 0$	s-subshell	2s
		$\ell = 1$	p-subshell	2p
n = 3	M-shell	$\ell = 0$	s-subshell	3s
		$\ell = 1$	p-subshell	3p
		$\ell = 2$	d-subshell	3d
n = 4	N-shell	$\ell = 0$	s-subshell	4s
		$\ell = 1$	p-subshell	4p
		$\ell = 2$	d-subshell	4d
		$\ell = 3$	f-subshell	4f

- Shells and sub-shells are occupied in energy-level order
- Electrons occupy orbitals singly to prevent any repulsion caused by pairing.

Total number of electrons

In 1s, 2s,......, etc. the digit represents the value of principal quantum number. 'ℓ' values also enable us to calculate the total number of electrons in a given subshell. The formula for calculating the electrons is $2(2\ell + 1)$.

$\ell = 0$ s-subshell total electrons = 2
$\ell = 1$ p-subshell total electrons = 6
$\ell = 2$ d-subshell total electrons = 10
$\ell = 3$ f-subshell total electrons = 14

(iii) Magnetic Quantum Number (m)

In the defects of Bohr's model, it has been mentioned that strong magnetic field splits the spectral lines further (Zeeman effect). In order to explain this splitting, a third quantum number called magnetic quantum number (m) has been proposed.

Values

$$m = 0, \pm1, \pm2, \pm3$$

Relationship between azimuthal and magnetic quantum numbers

The value of 'm' depends upon values of 'ℓ'

When $\ell = 0$ s-subshell $m = 0$
$\ell = 1$ p-subshell $m = 0, \pm1$ (p – subshell has three degenerate orbitals)
$\ell = 2$ d-subshell $m = 0, \pm1, \pm2$ (d – subshell has five degenerate orbitals)
$\ell = 3$ f-subshell $m = 0, \pm1, \pm2, \pm3$ (f – subshell has seven degenerate orbitals)

The above description shows that for a given value of 'ℓ', the total values of 'm' are $(2\ell + 1)$.

Degeneracy of orbitals

Actually the value of 'm' gives us the information of degeneracy of orbitals in space. It tells us the number of different ways in which a given s, p, d or f-shell can be arranged along x, y and z axes in the presence of magnetic field. Thus, different values of 'm' for a given value of 'ℓ', represent the total number of different **space orientations for a subshell.**

For s-subshell

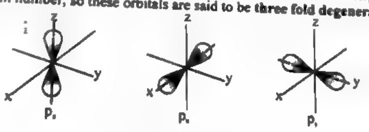
For s-subshell, $\ell = 0$, so $m = 0$. It implies that s-subshell of any energy level has only one space orientation and can be arranged in space only in one way along x, y and z-axes. So, s-subshell is not sub-divided into any other orbital

The shape of 's' orbital is such that probability of finding the electron in all the directions from the nucleus is the same. It is a spherical and symmetrical orbital.

For p-subshell

For p-subshell, $\ell = 1$, and $m = 0, \pm 1$. These values of 'm' imply that p-subshell of any energy level has three space orientations and can be arranged in space along x, y and z axes. These three orbitals are perpendicular to each other and named as p_x, p_y and p_z. They have egg shaped lobes which touch each other at the origin. They are disposed symmetrically along one of three axes called **orbital axis.**

In the absence of the magnetic field, all the three p-orbitals have the same energy and are called **degenerate orbitals**. Since, they are three in number, so these orbitals are said to be **three fold degenerate or triply degenerate.**

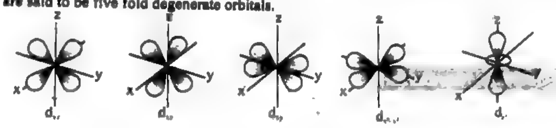


Shapes of p-orbitals

For d-subshell

For d-subshell, $\ell = 2$, $m = 0, \pm 1, \pm 2$. It implies that it has five space orientations and are designated as $d_{xy}(m = -2)$, $d_{yz}(m = -1)$, $d_{zx}(m = +1)$, $d_{x^2-y^2}(m = +2)$ and $d_{z^2}(m = 0)$.

All these five d-orbitals are not identical in shape. In the absence of a magnetic field, all five d-orbitals have the same energy and they are said to be five fold degenerate orbitals.



Shapes of d-orbitals

For f-subshell.

For f-subshell, $\ell = 3$ and $m = 0 \pm 1, \pm 2, \pm 3$. They have complicated shapes.

Since magnetic quantum number determines the orientation of orbitals, so it is also called **orbital orientation quantum number.**

> **Degenerate Orbitals**
>
> Orbitals which are located at the same energy level on the energy level diagram are called degenerate orbitals. Thus, electrons have equal probability to occupy any of the degenerate orbitals.
>
> p_x, p_y and p_z $\rightarrow$ 3-fold degenerate
>
> d-orbitals $\rightarrow$ 5-fold degenerate
>
> f-orbitals $\rightarrow$ 7-fold degenerate
>
> Degeneracy of p-orbitals remains unaffected in presence of external uniform magnetic field but degeneracy of d and f-orbitals is affected by external magnetic field.

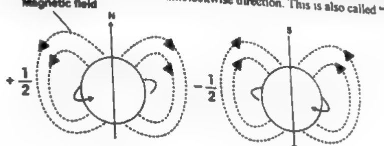
(iv) Spin Quantum Number(s)

Alkali metals have one electron in their outermost shell. We can record their emission spectra, when the outermost electron jumps from an excited state to a ground state. When the spectra are observed by means of high

resolving power spectrometer, each line in the spectrum is found to consist of a pair of lines, this is called **doublet line structure.**

Doublet line structure is different from fine spectrum of hydrogen. It should be made clear that lines of doublet line structure are widely separated from each other while those of fine structure are closely spaced together.

In 1925, Goudsmit and Uhlenbech suggested that an electron while moving in an orbital around the nucleus also rotates or spins about its own axis either in clockwise or anticlockwise direction. This is also called **"self-rotation."**



Clockwise spin motion is represented by $+\frac{1}{2}$

Anticlockwise spin motion is represented by $-\frac{1}{2}$

This spinning electron is associated with a magnetic field and hence a magnetic moment. Hence, opposite magnetic fields are generated by the clockwise and anticlockwise spins of electrons. This spin motion is responsible for doublet line structure in the spectrum.

Quantum Numbers of Electrons

Principal Quantum number 'n'	Azimuthal Quantum number ( )	Magnetic Quantum number (m)	Spin Quantum number (s)	Number of electrons accommodated
1 K	0 s	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2 L	0 s	0	$+\frac{1}{2}, -\frac{1}{2}$	2 } 8
	1 p	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$	6
3 M	0 s	0	$+\frac{1}{2}, -\frac{1}{2}$	2 } 18
	1 p	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$	6
	2 d	+2, +1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$	10
4 N	0 s	0	$+\frac{1}{2}, -\frac{1}{2}$	2 } 32
	1 p	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$	6
	2 d	+2, +1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$	10
	3 f	+3, +2, +1, 0, -1, -2, -3	$+\frac{1}{2}, -\frac{1}{2}$	14

Q.14c. When azimuthal quantum number has a value 3, then there are seven values of magnetic quantum number, give reasons.

Ans. Magnetic quantum number values are related to azimuthal quantum number as

$m = (2\ell + 1)$

as $\ell = 3$

Then $m = (2 \times 3 + 1) = 7$

as $\ell = 3$ and subshell is 'f'. This shows that f-subshell has 7 different ways of orientation in space because it has 7 values of magnetic quantum number

When $\ell = 3$, then $m = 0, \pm1, \pm2, \pm3 = 7$ values

(i) f_{x^3} (ii) f_{y^3} (iii) f_{z^3} (iv) f_{xyz} (v) $f_{x^2-y^2}$ (vi) $f_{y^2-z^2}$ (vii) $f_{x^2-z^2}$

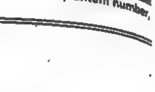
Q.16 Draw the shapes of s,p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

Shapes of Orbitals

We were introduced to the four types of orbitals depending upon the values of azimuthal quantum number. These orbitals are s, p, d and f having azimuthal quantum number values as $\ell = 0,1,2,3$ respectively. Let us, discuss the shapes of these orbitals

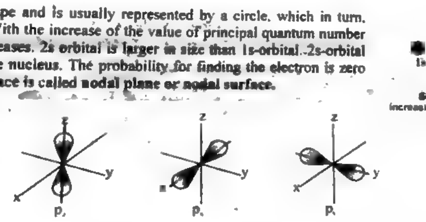
Shapes of s-Orbitals

s-orbital has a spherical shape and is usually represented by a circle, which in turn, represents a cut of sphere. With the increase of the value of principal quantum number (n), the size of s-orbital **increases. 2s orbital is larger in size than 1s-orbital.** 2s-orbital is also further away from the nucleus. The probability for finding the electron is zero between two orbitals. **This place is called nodal plane or nodal surface.**



Shapes of s-orbitals with increasing principal quantum number

Shapes of p-Orbitals



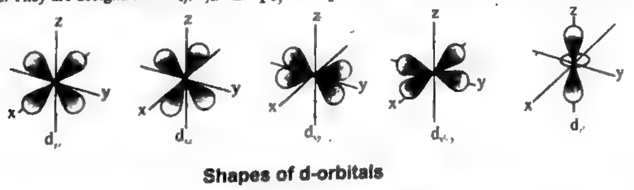
Shapes of p-orbitals

p-subshell has three values of magnetic quantum number. So p-subshell has three orientations in space i.e., along x, y and z axes. All the three p-orbitals namely p_x, p_y and p_z have dumb-bell shapes. So

p-orbitals have directional character which determines the geometry of molecules. All the p-orbitals of all the energy levels have the similar shapes, but with the increase of principal quantum number of the shell their sizes are increased.

Shapes of d-Orbitals

d-subshell have five values of magnetic quantum number. So there are five space orientations along x, y and z axes. They are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}. The lobes of first three d-orbitals lie between the axes.



Shapes of d-orbitals

The other lie on the axes .They are not identical in shape. Four d-orbitals have four lobes while fifth d-orbital called d_{z^2} consists of only two lobes.

In the absence of magnetic field, all the five d-orbitals are degenerate.

ELECTRONIC DISTRIBUTION

In order to understand the distribution of electrons in an atom, we should know the following facts:

(1) An orbital like s, p_x, p_y, p_z, d_{xy} etc. can have at the most two electrons.

(2) The maximum number of electrons than can be accommodated in a shell is given by $2n^2$ where n is the principal quantum number and it cannot have zero value.

(3) Maximum number of electrons in sub-shells are given as s = 2, p = 6, d = 10, f = 14

Moreover following rules are used for the distribution of electrons in sub-shells or orbitals:

(i) Auf-bau principle
(ii) Pauli exclusion principle
(iii) Hund's Rule

Before we use these rules the subshells or orbitals should be arranged according to $(n + \ell)$ rule also called Wiswesser's rule.

Arrangement of orbitals according to $(n + \ell)$ rule

Orbital	n	ℓ	$n + \ell$
1s	1	0	1 + 0 = 1
2s	2	0	2 + 0 = 2
2p	2	1	2 + 1 = 3
3s	3	0	3 + 0 = 3
3p	3	1	3 + 1 = 4
3d	3	2	3 + 2 = 5
4s	4	0	4 + 0 = 4
4p	4	1	4 + 1 = 5
4d	4	2	4 + 2 = 6
4f	4	3	4 + 3 = 7
5s	5	0	5 + 0 = 5
5p	5	1	5 + 1 = 6
5d	5	2	5 + 2 = 7
5f	5	3	5 + 3 = 8
6s	6	0	6 + 0 = 6
6p	6	1	6 + 1 = 7
6d	6	2	6 + 2 = 8
6f	6	3	6 + 3 = 9
7s	7	0	7 + 0 = 7
7p	7	1	7 + 1 = 8
7d	7	2	7 + 2 = 9
7f	7	3	7 + 3 = 10
8s	8	0	8 + 0 = 8

Wiswesser's $(n + \ell)$ rule

Subshells are arranged in the increasing order of $(n+\ell)$ values and if any two subshells have the same $(n+\ell)$ values, then that subshell is placed first whose n value is smaller.

So, the arrangement of subshells or orbitals in the order of increasing energy values (ascending order) is as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s

Auf bau Principle

This principle states, the electrons should be filled in energy subshells in order of increasing energy values. The electrons are first placed in 1s, 2s, 2p and so on.

Pauli's Exclusion Principle

This principle can be stated as follows:

"It is impossible for two electrons residing in the same orbital of a poly-electron atom to have the same values of four quantum numbers."

or

"Two electrons in the same orbital should have opposite spins (↓↑)".

- Each electron is shown as an arrow, indicating its spin: either ↓ or ↑
- Within an orbital, the electrons must have opposite spins

allowed

↑↓ ↓↑

not allowed

↑↑ ↓↓

Example

Consider an electron occupying 1s orbital. For this electron $n = 1$, $\ell = 0$, $m = 0$. Suppose the electron under consideration has $s = +1/2$ which is indicated by ↑. Now if another electron is put in the same 1s orbital. For this electron $n = 1$, $\ell = 0$, $m = 0$. It can occupy the same 1s orbital only if the direction of spin of this electron is opposite to that of the first electron i.e., $s = -1/2$ symbolized as ↓.

Since, there are only two possible values for s. So one orbital may contain a maximum of two electrons only when the direction of spin of one is opposite to that of other.

Hund's Rule

According to this rule

"If, degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins."

By using this rule, the distribution of electrons in sub-shells of C, N and O are as follows

$$_6C = \overset{\uparrow\downarrow}{1s},\ \overset{\uparrow\downarrow}{2s},\ \overset{1}{2p_x},\ \overset{1}{2p_y},\ \overset{0}{2p_z}$$

$$_7N = \overset{\uparrow\downarrow}{1s},\ \overset{\uparrow\downarrow}{2s},\ \overset{1}{2p_x},\ \overset{1}{2p_y},\ \overset{1}{2p_z}$$

$$_8O = \overset{\uparrow\downarrow}{1s},\ \overset{\uparrow\downarrow}{2s},\ \overset{\uparrow\downarrow}{2p_x},\ \overset{1}{2p_y},\ \overset{1}{2p_z}$$

Element	Atomic number	Electron Configuration Notation
Hydrogen	1	$1s^{\uparrow}$
Helium	2	$1s^2$
Lithium	3	$1s^2 2s^{\uparrow}$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^{\uparrow}, 2p, 2p$
Carbon	6	$1s^2 2s^2 2p^{\uparrow}, 2p^{\uparrow}, 2p$
Nitrogen	7	$1s^2 2s^2 2p^{\uparrow}, 2p^{\uparrow}, 2p^{\uparrow}$
Oxygen	8	$1s^2 2s^2 2p^2, 2p^{\uparrow}, 2p^{\uparrow}$
Fluorine	9	$1s^2 2s^2 2p^2, 2p^2, 2p^{\uparrow}$
Neon	10	$1s^2 2s^2 2p^2, 2p^2, 2p^2$
Sodium	11	$[Ne].\ 3s^{\uparrow}$
Magnesium	12	$[Ne].\ 3s^{\uparrow\downarrow}$
Aluminum	13	$[Ne].\ 3s^2 3p^{\uparrow}, 3p, 3p$
Silicon	14	$[Ne].\ 3s^2 3p^{\uparrow}, 3p^{\uparrow}, 3p$
Phosphorus	15	$[Ne].\ 3s^2 3p^{\uparrow}, 3p^{\uparrow}, 3p^{\uparrow}$
Sulphur	16	$[Ne].\ 3s^2 3p^2, 3p^{\uparrow}, 3p^{\uparrow}$
Chlorine	17	$[Ne].\ 3s^2 3p^2, 3p^2, 3p^{\uparrow}$
Argon	18	$[Ne].\ 3s^2 3p^2, 3p^2, 3p^2$

Element	Atomic number	Electron Configuration Notation
Potassium	19	$[Ar].\ 4s^{\uparrow}$
Calcium	20	$[Ar].\ 4s^2$
Scandium	21	$[Ar].\ 4s^2 3d^{\uparrow}, 3d, 3d, 3d, 3d$
Titanium	22	$[Ar].\ 4s^2 3d^{\uparrow}, 3d^{\uparrow}, 3d, 3d, 3d$
Vanadium	23	$[Ar].\ 4s^2 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}, 3d, 3d$
Chromium	24	$[Ar].\ 4s^{\uparrow} 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}$
Manganese	25	$[Ar].\ 4s^2 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}$
Iron	26	$[Ar].\ 4s^2 3d^2, 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}$
Cobalt	27	$[Ar].\ 4s^2 3d^2, 3d^2, 3d^{\uparrow}, 3d^{\uparrow}, 3d^{\uparrow}$
Nickel	28	$[Ar].\ 4s^2 3d^2, 3d^2, 3d^2, 3d^{\uparrow}, 3d^{\uparrow}$
Copper	29	$[Ar].\ 4s^{\uparrow} 3d^2, 3d^2, 3d^2, 3d^2, 3d^2$
Zinc	30	$[Ar].\ 4s^2 3d^2, 3d^2, 3d^2, 3d^2, 3d^2$
Gallium	31	$[Ar].\ 4s^2 3d^{10} 4p^{\uparrow}, 4p, 4p$
Germanium	32	$[Ar].\ 4s^2 3d^{10} 4p^{\uparrow}, 4p^{\uparrow}, 4p$
Arsenic	33	$[Ar].\ 4s^2 3d^{10} 4p^{\uparrow}, 4p^{\uparrow}, 4p^{\uparrow}$
Selenium	34	$[Ar].\ 4s^2 3d^{10} 4p^2, 4p^{\uparrow}, 4p^{\uparrow}$
Bromine	35	$[Ar].\ 4s^2 3d^{10} 4p^2, 4p^2, 4p^{\uparrow}$
Krypton	36	$[Ar].\ 4s^2 3d^{10} 4p^2, 4p^2, 4p^2$

Some exceptional electronic configurations

Chromium (Atomic number = 24) :

Expected configuration : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$

Actual configuration : $1s^2 2s^2 2p^6 3p^6 3d^5 4s^1$

Copper (Atomic number = 29) :

Expected configuration : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$

Actual configuration . $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Molybdenum (Atomic number = 42)

Expected configuration · $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^4 5s^2$

Actual configuration . $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^1$

Palladium (Atomic number = 46)

Expected configuration . $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^8 5s^2$

Actual configuration · $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^0$

In electronic configuration of any element if outermost shell contain following order than changes occur's in following manner for stability

s, d ⟶ d, s

s, d, p ⟶ d, s, p

s, f ⟶ f, s

s, f, d, p ⟶ f, d, s, p

$d^4s^2 \longrightarrow d^5s^1$

$d^9s^2 \longrightarrow d^{10}s^1$

of greater stability of exactly half-filled and completely filled configurations

The greater stability of these configurations is due to the following two reasons .

(i) Symmetry.

The half-filled and completely filled configurations are more symmetrical and symmetry leads to greater stability.

(ii) Exchange energy.

The electrons present in the different orbitals of the same subshell can exchange their positions Each such exchange leads to a greater stability which can be explained in terms of exchange energy. As the number of exchanges that can take place is maximum in the exactly half-filled and completely filled arrangements (i.e. more in d^5 than in d^4 and more in d^{10} than in d^9), therefore exchange energy is maximum and hence the stability is maximum.

Some important points in writing electronic configurations

While writing the electronic configurations, the following points may also be noted:

(i) To avoid the writing of electronic configurations in a lengthy way, usually the symbols $[He]^2$, $[Ne]^{10}$, $[Ar]^{18}$ etc. are used as the first part of the configuration. Such a symbol stands for the electronic configuration of that inert gas and is usually called the core of the inert gas.

(ii) Although the orbitals of lower energy are filled first but the electronic configuration are written not in the order in which the orbitals were filled but in the order of principal quantum numbers.

(iii) Unless otherwise mentioned, electronic configuration always means the electronic configuration in the ground state.

(iv) Always remember that if you write down electronic configuration of ion (cation or anion), than first you write configuration of basic atom than add or remove the electron from the system otherwise always there is a chance of error.

KEY POINTS

1. Matter is made up of extremely small particles called atoms.
2. Cathode rays and positive rays were discovered during discharge tube experiments. The properties of cathode rays showed them to be negatively charged particles called electrons, whereas, the positive rays were found to contain positively charged particles called protons.
3. Neutron was discovered through artificial radioactivity.
4. Electrons, protons and neutrons are regarded as the fundamental particles of an atom.
5. Rutherford discovered the nucleus and successfully explained the presence of moving electrons around the nucleus.
6. In 1905, Planck put forward his famous Planck's quantum theory.
7. Neil Bohr explained the structure of hydrogen atom by using Planck's quantum theory. He also calculated the radius and energy of electron in the n^{th} shell of hydrogen atom.
8. Bohr's atomic model successfully explained the origin of line spectrum and the lines present in the spectrum of hydrogen atom in the visible and invisible regions.
9. X-rays are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube.
10. Moseley discovered a simple relationship between the frequency of X-rays and the atomic number of the target element.
11. de-Broglie discovered wave particle duality of material particles. According to him all material particles in motion have a dual character. Davisson and Germer experimentally verified the wave concept of an electron.
12. Heisenberg pointed out that it is not possible for us, to measure the exact position and the exact momentum of electron simultaneously.

13 After the failure of Bohr's atomic model, Schrodinger developed the wave mechanical model of hydrogen atom. According to him, although the position of an electron cannot be found exactly, the probability of finding an electron at a certain position at any time can be calculated.

14. An electron in an atom is completely described by its four quantum numbers. Three out of these four quantum numbers, have been derived from Schrodinger wave equation, when it is solved for hydrogen atom.

SOLVED OBJECTIVE EXERCISE

Q1. Select the most suitable answer for the given one:

(i) The nature of the positive rays depend on.
(a) the nature of the electrode (b) the nature of the discharge tube
(c) the nature of residual gas (d) all of the above

(ii) The velocity of photon is:
(a) independent of its wavelength (b) depends on its wavelength
(c) equal to square of its amplitude (d) depends on its source

(iii) Wave number of the light emitted by a certain source is $2 \times 10^6\ m^{-1}$. The wavelength of this light will be.
(a) 500 nm (b) 500 m
(c) 200 nm (d) 5×10^7 m

(iv) Rutherford's model of atom failed because:
(a) the atom did not have a nucleus and electrons
(b) it did not account for the attraction between protons and neutrons
(c) it did not account for the stability of the atom
(d) there is actually no space between the nucleus and the electrons

(v) Bohr's model of atom is contradicted by:
(a) Planck's quantum theory (b) Dual nature of matter
(c) Heisenberg's uncertainty principle (d) All of the above

(vi) Splitting of spectral lines when atoms are subjected to strong electric field is called:
(a) Zeeman effect (b) Stark effect
(c) Photoelectric effect (d) Compton effect

(vii) In the ground state of an atom, the electron is present:
(a) in the nucleus (b) in the second shell
(c) nearest to the nucleus (d) farthest from the nucleus

(viii) Quantum number values for 2p orbitals are:
(a) $n = 2, \ell = 1$ (b) $n = 1, \ell = 2$
(c) $n = 1, \ell = 0$ (d) $n = 2, \ell = 0$

(ix) Orbitals having same energy are called:
(a) hybrid orbitals (b) valence orbitals
(c) degenerate orbitals (d) d-orbitals

(x) When 6d orbital is complete, the entering electron will go to:
(a) 7f (b) 7s
(c) 7p (d) 7d

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(c) the nature of residual gas	Positive rays are produced by the ionization of a gas in the discharge tube. Different gases have different nature of positive rays.
(ii)	(a) independent of its wavelength	The velocity of electromagnetic radiation (light) is $3 \times 10^8\ ms^{-1}$. The components of white light have different wave lengths
(iii)	(a) 500 nm	$\bar{\upsilon} = \frac{1}{\lambda}$ $\lambda = \frac{1}{\bar{\upsilon}}$
(iv)	(c) it did not account for the stability of the atom	Atom is stable particle but Rutherford failed to explain its stability
(v)	(c) Heisenberg's uncertainty principle	In Bohr's atom, the electrons are moving with specific velocities in orbits of specified radii, and according to uncertainty principle, both these quantities cannot be measured experimentally. A theory involving quantities, which cannot be measured, does not follow the tradition of scientific work
(vi)	(b) Stark effect	When the excited hydrogen atoms are placed in an electrical field, its spectral lines are further split up into closely spaced lines. This type of splitting of spectral lines is called "**Stark effect.**"
(vii)	(c) nearest to the nucleus	Ground state is a stable state for an atom at this state electron is present nearest to the nucleus. At this state the system has highest stability.
(viii)	(a) $n = 2, \ell = 1$	For 2p, n = 2 (L shell) and $\ell = 1$ (p sub shell)
(ix)	(c) degenerate orbitals	$2p_x$, $2p_y$ and $2p_z$ are degenerate orbitals.
(x)	(c) 7p	1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s

Q2. Fill in the blanks with suitable words:

(i) β-particles are nothing but ________ moving with a very high speed.
(ii) Charge on one mole of electrons is ________ coulombs.
(iii) The mass of Hydrogen atom is ________ grams.
(iv) The mass of one mole electrons is ________.
(v) Energy is ________ when electron jumps from higher to a lower orbit.
(vi) The ionization energy of hydrogen atom can be calculated from ________ model of atom.
(vii) For d-subshell, the azimuthal quantum number has a value of ________.
(viii) The number of electrons in a given sub-shell is given by formula ________.
(ix) Electronic configuration of H^- is ________.

ANSWERS

(i) electrons	(ii) 96484 C
(iii) 1.67×10^{-24}	(iv) 5.48×10^{-4} g or 0.54 mg
(v) emitted	(vi) Bohr's
(vii) 2	(viii) $2(2\ell + 1)$
(ix) $1s^2$	

Q3. Indicate true or false as the case may be:

(i) A neutron is slightly lighter particle than a proton.
(ii) A photon is a massless bundle of energy but has momentum.
(iii) The unit of Rydberg constant is the reciprocal of unit of length.
(iv) The actual isotopic mass is a whole number.
(v) Heisenberg's uncertainty principle is applicable to macroscopic bodies.
(vi) The nodal plane in an orbital is the plane of zero electron density.

(vii) The number of orbitals present in a sublevel is given by the formula $(2\ell + 1)$.

(viii) The magnetic quantum number was introduced to explain Zeeman effect and Stark effect.

(ix) Spin quantum number tells us the direction of spin of electron around the nucleus.

ANSWERS

(i) False	(ii) True	(iii) True	(iv) False	(v) False
(vi) True	(vii) True	(viii) False	(ix) False	

SHORT ANSWERS TO EXERCISE

Q.15 (b)

Ans. ***(n + l) Rule***

"n" is a principle quantum number while "l" is azimuthal quantum number. (n + l) rule means a rule based on sum of principle quantum number value and azimuthal quantum number value of subshell

Statement

Subshell are arranged in the increasing order of (n + l) values and if any two subshell have the same (n + l) values, then that subshell is placed first whose value is smaller.

Arrangement of Subshell

According to (n + l) rule the arrangement of subshell is

1s< 2s <2p <3s <3p <4s <3d <4p, <5s <4d <5p <6s < 4f <5d <6p <7s

(n + l) rule and degenerate orbitals

Those orbitals which have same energy are called degenerate orbitals.

(n + l) rule is not applicable to degenerate orbitals because they have same values of n and l.

For example: There are three degenerate orbitals of 2p subshell, 2px, 2py, 2pz. These three orbitals of 2p subshell have n = 2 and l = 1 their (n + l) value are same that is three.

The degeneracy of orbitals is explained by magnetic quantum not by principle quantum number or azimuthal quantum number To fill degenerate orbitals Hund's rule is applied.

Q.15 (c)

Ans. ***Distribution of electron in orbitals***

$_{57}La = 57 = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,6s^2\,4f^0\,5d^1$

$_{29}Cu = 29 = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,\overset{\uparrow}{4s}\ \overset{\uparrow\downarrow}{3d_{xy}}\ \overset{\uparrow\downarrow}{3d_{yz}}\ \overset{\uparrow\downarrow}{3d_{xz}}\ \overset{\uparrow\downarrow}{3d_{x^2-y^2}}\ \overset{\uparrow\downarrow}{3d_{z^2}}$

$_{79}Au = 79 = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,\overset{\uparrow}{6s}\ 4f^{14}\ \overset{\uparrow\downarrow}{5d_{xy}}\ \overset{\uparrow\downarrow}{5d_{yz}}\ \overset{\uparrow\downarrow}{5d_{xz}}\ \overset{\uparrow\downarrow}{5d_{x^2-y^2}}\ \overset{\uparrow\downarrow}{5d_{z^2}}$

$_{24}Cr = 24 = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,\overset{\uparrow}{4s}\ \overset{\uparrow}{3d_{xy}}\ \overset{\uparrow}{3d_{yz}}\ \overset{\uparrow}{3d_{xz}}\ \overset{\uparrow}{3d_{x^2-y^2}}\ \overset{\uparrow}{3d_{z^2}}$

$_{53}I = 53 = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,\overset{\uparrow\downarrow}{5p_x}\ \overset{\uparrow\downarrow}{5p_y}\ \overset{\uparrow}{5p_z}$

$_{86}Rn = 86 = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,6s^2\,4f^{14}\,5d^{10}\,\overset{\uparrow\downarrow}{6p_x}\ \overset{\uparrow\downarrow}{6p_y}\ \overset{\uparrow\downarrow}{6p_z}$

NUMERICALS OF EXERCISE

Q.17. (a) **A photon of light with energy 10^{-19} Joules is emitted by a source of light. Convert this energy into the wavelength, frequency and wave number of the photon in terms of meter, hertz and m^{-1}, respectively.**

Ans. **Given data:**

Energy of photon $E = 10^{-19}$ joules

Required:

Wavelength $= \lambda = ?$

Frequency $= \upsilon = ?$

Wave number $= \bar{\upsilon} = ?$

Solution:

$E = h\upsilon$

(i) Frequency:

$$\upsilon = \frac{E}{h} \quad [\because h = 6.625 \times 10^{-34}\ Js]$$

$$\upsilon = \frac{10^{-19}\ J}{6.625 \times 10^{-34}\ Js}$$

$= 1.51 \times 10^{14}\ s^{-1}$ or Hertz.

(ii) Wavelength:

$$E = \frac{hc}{\lambda} \quad [c = \text{Velocity of light} = 3 \times 10^8\ ms^{-1}]$$

$$\lambda = \frac{6.625 \times 10^{-34}\ Js \times 3 \times 10^8\ ms^{-1}}{10^{-19}\ J} = 1.98 \times 10^{-6}\ m$$

(iii) $v = c\bar{\upsilon}$ so $E = hc\bar{\upsilon}$ or $\bar{\upsilon} = \frac{E}{hC}$

$$\bar{\upsilon} = \frac{10^{-19}\ J}{6.625 \times 10^{-34}\ Js \times 3 \times 10^8\ ms^{-1}} = 5 \times 10^5\ m^{-1}$$

Frequency : 1.51×10^{14} Hertz

Wavelength : 1.98×10^{-6} m

Wave number : $5 \times 10^5\ m^{-1}$

Q.17(b). **Convert the energy of (17a) into ergs and calculate the wavelength in cm, frequency in Hertz and wave number in cm^{-1}.**

Ans. **Given data:**

$E = 10^{-19}\ J$ $[1\ J = 10^7\ ergs]$

So $E = 10^{-19} \times 10^7$ ergs

Speed of light $c = 3 \times 10^8\ ms^{-1}$ $[1\ m = 10^2\ cm]$

$c = 3 \times 10^{10}\ cms^{-1}$

$h = 6.625 \times 10^{-34}\ Js$ $[1\ J = 10^7\ ergs]$

$h = 6.625 \times 10^{-34} \times 10^7$ erg.s.

Requirement:

λ in cm = ?

υ in Hertz = ?
$\bar{\upsilon}$ in cm^{-1} = ?
Solution:

$$E = h\upsilon, \qquad E = \frac{hc}{\lambda}, E = hc\bar{\upsilon}$$

(i) Frequency:

$$\upsilon = \frac{E}{h}$$

$$= \frac{10^{-19} \times 10^{7} \text{ ergs}}{6.625 \times 10^{-34} \times 10^{7} \text{ ergs.s.}}$$

$$= 1.51 \times 10^{14} s^{-1}$$

(ii) Wavelength:

$$\lambda = \frac{hc}{E}$$

$$= \frac{6.625 \times 10^{-34} \times 10^{7} \text{ ergs.s} \times 3 \times 10^{10} \text{ cms}^{-1}}{10^{-19} \times 10^{7} \text{ ergs.}}$$

$$= 1.98 \times 10^{-4} \text{ cm}$$

(iii) Wave number:

$$\bar{\upsilon} = \frac{E}{hc}$$

$$\bar{\upsilon} = \frac{10^{-19} \times 10^{7} \text{ ergs}}{6.625 \times 10^{-34} \times 10^{7} \text{ ergs.s} \times 3 \times 10^{10} \text{ cms}^{-1}}$$

$$= 5 \times 10^{3} \text{ cm}^{-1}$$

Frequency : $1.51 \times 10^{14} s^{-1}$
Wavelength : 1.98×10^{-4} cm
Wave number : $5 \times 10^{3} cm^{-1}$

Q18. ***The formula for calculating the energy of an electron in hydrogen atom is given by Bohr's model.***

$$En = \frac{-m^2e^4}{8\varepsilon_o^2h^2n^2}$$

Calculate the energy of the electron in first orbit of hydrogen atom.

Ans. **Given data:**
$m = 9.1095 \times 10^{-31}$ kg
$e = 1.6022 \times 10^{-19}$ C
$\varepsilon_o = 8.84 \times 10^{-12} C^2J^{-1}m^{-1}$
$h = 6.625 \times 10^{-34}$ Js
$n = 1$
Requirement:
$E_n = ?$
Solution:

$$E_n = \frac{-m^2e^4}{8\varepsilon_o^2h^2n^2},$$

by putting the values.

$$E_n = \frac{-(9.1095 \times 10^{-31} kg)^2(1.6022 \times 10^{-19} C)^4}{8(8.84 \times 10^{-12} C^2J^{-1}m^{-1})^2(6.625 \times 10^{-34} Js)^2(1)^2}$$

$$-2.178 \times 10^{18} \text{ Joules}$$

Q19. **Bohr's equation for radius is $r_n = \frac{\epsilon_o h^2n^2}{\pi me^2}$ for hydrogen atom. When its electron moves from n = 1 to n = 2, how much does radius of the orbit increases.**

Ans. **Given data:**
Lower orbit, n = 1 is r_1
Higher orbit, n = 2 is r_2
Requirement:
$r_2 - r_1 = ?$
Solution:
Bohr's equation for radius is $r_n = 0.529\ n^2$ Å for hydrogen atom
So

$$r_1 = 0.529 \times 1^2 = 0.529 \text{ Å}$$

$$r_2 = 0.529 \times 2^2 = 2.11 \text{ Å}$$

$$\therefore \quad r_2 - r_1 = 2.11 - 0.529 = 1.58 \text{ Å}$$

Increase in radius is 1.58 Å

Q19b. **What is distance travelled by electron when it goes from n = 2 to n = 3, and n = 9 to n = 10 for hydrogen atom.**

Ans. **Given data:**
Number of orbits n = 2, 3, 9, 10
So radii to be calculated are r_2, r_3, r_9, r_{10}
Requirement:
$r_3 - r_2 = ?$
$r_{10} - r_9 = ?$
Solution:
Equation for radius = $0.529\ n^2$ Å (for hydrogen atom)

$$r_2 = 0.529 \times 2^2 = 2.11 \text{ Å} \ (1 \text{ Å} = 10^{-10} \text{ m})$$

$$r_3 = 0.529 \times 3^2 = 4.75 \text{ Å}$$

$$\therefore \quad r_3 - r_2 = 4.75 - 2.11 = 2.64 \text{ Å}$$

Similarly,

$$r_9 = 0.529 \times 9^2 = 42.85 \text{ Å}$$

$$r_{10} = 0.529 \times 10^2 = 52.9 \text{ Å}$$

$$\therefore \quad r_{10} - r_9 = 52.9 - 42.85 = 10.05 \text{ Å}$$

(i) Distance travelled from n = 2 to n = 3 is 2.64 Å
(ii) Distance travelled from n = 9 to n = 10 is 10.05 Å

Q. 20 (a)

Ans. The formula of energy of an electron of hydrogen atom is

$$E_n = -2.18\times10^{-18}\left[\frac{1}{n^2}\right]J$$

where "n" is the number of orbit

Energy of first orbit

n = 1

$$E_1 = -2.18\times10^{18}\times\frac{1}{1^2} = -2.18\times10^{18}\,j$$

Energy of second orbit

n = 2

$$E_2 = -2.18\times10^{-18}\left(\frac{1}{2^2}\right)$$

$$= -2.18\times10^{-18}\times\frac{1}{4} = -0.545\times10^{-18}\,j$$

Energy of third orbit

n = 3

$$E_3 = -2.18\times10^{18}\left(\frac{1}{3^2}\right)$$

$$= -2.18\times10^{-18}\times\frac{1}{9} = -0.242\times10^{-18}\,j$$

Energy of forth orbit

n = 4

$$E_4 = -2.18\times10^{-18}\left(\frac{1}{4^2}\right)$$

$$= -2.18\times10^{-18}\times\frac{1}{16} = -0.14\times10^{-18}\,j$$

Energy of Fifth orbit

n = 5

$$E_5 = -2.18\times10^{-18}\left(\frac{1}{5^2}\right)$$

$$= -2.18\times10^{-18}\times\frac{1}{25} = -0.08\times10^{-18}\,j$$

Q.20 (b)

Ans. The Bohr's equation for hydrogen atom is

$$E_n = -\frac{1313.315}{n^2}\ \text{kjmole}^{-1}$$

We can calculate energy for first, second and third orbit of hydrogen with the help of above equation energy of first orbit (E_1)

$$E_1 = -\frac{1313.315}{(1)^2} = -1313.315\text{kjmole}^{-1}$$

Energy of second orbit (E_2)

$$E_2 = -\frac{1313.315}{(2)^2} = -328.32\text{kjmole}^{-1}$$

Energy of third orbit (E_3)

n = 3

$$E_3 = -\frac{1313.315}{(3)^2} = -145.92\text{kjmole}^{-1}$$

Energy difference between first and second orbit

$$E_2 - E_1 = (-328.32)-(-1313.315)$$

$$-328.32+1313.315 = 984.99\text{kjmole}^{-1}$$

Energy difference between second and third orbit

$$E_3 - E_2 = (-145.92)-(-328.32)$$

$$= -145.92+328.32 = 182.4\text{kjmole}^{-1}$$

Comparison between energy differences

$$E_2 - E_1 : E_3 - E_2$$

$$984.99 : 182.40$$

$$\frac{984.99}{182.40} : \frac{182.40}{182.40}$$

$$5.4 : 1$$

This show that energy difference between second and third orbit of hydrogen atom is approximately five time smaller than that between first and second orbits.

Q.20 (c)

Ans. **Given data**

Atomic Number of $He^+ = Z = 2$

Required

(i) Energy of first five orbit of H^+ = ?

(ii) Energy differences between orbits = ?

Solution

According to Bohr's equation

$$E_n = -1313.315\times\frac{Z^2}{n^2}\ \text{kjmole}^{-1}$$ (For any atom of unieletronic system)

Energy of first five orbits of He^+

Energy of first orbit

n = 1

$$E_1 = -1313.315\times\frac{(2)^2}{(1)^2}$$

$$E_1 = -1313.315\times4 = -5253.2\text{kjmole}^{-1}$$

Energy of second orbit

n = 2

$$E_2 = -1313.315\times\frac{(2)^2}{(2)^2}$$

$$E_2 = -1313..15\times1 = -1313.315\text{kjmole}^{-1}$$

Energy of third orbit

n = 3

$$E_2 = -1313.315 \times \frac{(2)^2}{(3)^2}$$

$$E_3 = -1313.315 \times \frac{4}{9} = -583.69\,\text{kjmole}^{-1}$$

Energy of 4^{th} orbit

$n = 4$

$$E_4 = -1313.315 \times \frac{(2)^2}{(4)^2}$$

$$E_4 = -1313.315 \times \frac{4}{16} = -328.325\,\text{kjmole}^{-1}$$

Energy of 5^{th} orbit

$n = 5$

$$E_5 = -1313.315 \times \frac{(2)^2}{(5)^2}$$

$$= -1313..15 \times \frac{4}{25} = -210.1304$$

Energy differences between different orbits of He^+

$$E_2 - E_1 = (-1313.315) - (-5253.2)$$
$$= -1313.315 + 5253.2 = 3939.885\,\text{kjmole}^{-1}$$
$$E_3 - E_2 = (-583.69) - (-1313.315)$$
$$= -583.69 + 1313.315 = 729.625\,\text{kjmole}^{-1}$$
$$E_4 - E_3 = (-328.325) - (-583.69)$$
$$= -328.325 + 583.69 = 255.365\,\text{kjmole}^{-1}$$
$$E_5 - E_4 = 210.1304 - (-328.325)$$
$$= -210.1304 + 328.325 = +118.194\,\text{kjmole}^{-1}$$

show that energy differences between different orbits of He^+ are different from those of hydrogen atom.

(d)

The energy difference between different orbits of He^+ are different than those of different orbits of hydrogen atom, therefore the position of spectral lines of He^+ will be at different places than those for hydrogen atom. The energy of each spectral line of He^+ will be greater than those of hydrogen atom when transiton take place from $n_2 = 2$ to $n_1 = 1$ or from $n_2 = 3$ to $n_1 = 2$.

Calculate the value of principle quantum number if electron of hydrogen atom revolves in an orbit of energy -0.242×10^{-18} J.

Given data:

Energy of orbit $E_n = -0.242 \times 10^{-18}$ J

Requirement:

$n = ?$

Solution:

$$E_n = -2.18 \times 10^{-18} \left(\frac{1}{n^2}\right) J$$

Put the value of E_n

$$-0.242 \times 10^{-18}\,J = \frac{-2.18 \times 10^{-18}}{n^2} J$$

$$n^2 = \frac{-2.18 \times 10^{-18} J}{-0.242 \times 10^{-18} J}$$

$$n^2 = 9$$

$$\sqrt{n^2} = \sqrt{9}$$

$$n = 3 \text{ Ans.}$$

So electron is in 3rd orbit of hydrogen-atom.

Q. $E_n = -K\left[\frac{Z^2}{n^2}\right]$

Thinking that $K = 2.18 \times 10^{-18}$ J. Calculate the energy needed to remove electron from Hydrogen atom and from He^+.

Ans. Given data:

$K = 2.18 \times 10^{-18}$ J

Atomic number of $He^+ = Z = 2$

Atomic number of H $= Z = 1$

Requirement:

Energy required to remove electron from He^+ = ?

Energy required to remove electron from H = ?

It is abbreviated as I.E.

Solution:

(i) $En = -K\left[\frac{Z^2}{n^2}\right]$

(ii) $E_\infty - E_1 = \text{I.E.}$

(i) For hydrogen atom

$$E_1 = -2.18 \times 10^{-18}\left[\frac{1}{1^2}\right] J$$
$$= -2.18 \times 10^{-18} \text{ Joules}$$
$$E_\infty = -2.18 \times 10^{-18}\left[\frac{1}{\infty^2}\right] J$$
$$= 0 \text{ Joules}$$

Energy required to remove electron from hydrogen atom $= E_\infty - E_1 = (0) - (-2.18 \times 10^{-18} J)$
$= 2.18 \times 10^{-18}$ J

(ii) For He^+

$$E_1 = \frac{-2.18 \times 10^{-18} \times 2^2 J}{1^2} = -8.72 \times 10^{-18} J$$

$$E_\infty = -2.18 \times 10^{-18} \times \frac{2^2}{\infty^2} J = 0 J$$

Energy required to remove electron from $He^+ = E_\infty - E_1 = 0 - (-8.72 \times 10^{-18} J)$
$= 8.27 \times 10^{-18}$ Joules

Energy required to remove electron from hydrogen atom $= 2.18 \times 10^{-18}$ Joules

Energy required to remove electron from He^+ $= 8.72 \times 10^{-18}$ Joules

Q22c. How do you justify that these energies are ionization potentials?

Ans. Ionization energy is "The minimum amount of energy required to remove an electron from isolated gaseous atom to form gaseous positive ion."

So 2.18×10^{-18} J, 8.72×10^{-18} J are ionization energies of Hydrogen and He^+ respectively.

Q22d. Use Avogadro's number to convert ionization energy values in kJ mol⁻¹ for H, He⁺.

Ans. **Given data:**

I.E. of H atom = 2.18×10^{-18} J

I.E. of He^+ ion = 8.72×10^{-18} J

Requirement:

I.E. in kJ mol^{-1} = ?

Solution:

If we multiply the energy with N_A and divide with 1000 their unit will become kJ mol^{-1}. So

Ionization energy of H-atom $= \dfrac{2.18\times10^{-18}\times6.02\times10^{23}}{1000} = 1313.31 \text{ kJ mol}^{-1}$

Ionization energy of He^+ ion $= \dfrac{8.72\times10^{-18}\times6.02\times10^{23}}{1000} = 5249.4 \text{ kJ mol}^{-1}$

Ionization energy of H $= 1313.31 \text{ kJmol}^{-1}$

Ionization energy of He^+ $= 5249.4 \text{ kJmol}^{-1}$

Q22e. The experimental value of ionization energy of H and He^+ are 1331 and 5250 respectively? How do you compare your answer with these values?

Ans. Theoretical values: Ionization energy of H = 1313.3 kJ mol^{-1}

Ionization energy of He^+ = 5249.4 kJ mol^{-1}

Experimental values: Ionization energy of H = 1331 kJ mol^{-1}

Ionization energy of He^+ = 5250 kJ mol^{-1}

Comparison: Both experimental and theoretical values are very close to each other.

Q23. Calculate the wave number of photon, when the electron jump from
(i) n = 5 to n = 2, (ii) n = 5 to n = 1
In which series of spectral lines and spectral regions these photons will appear.

Ans. **Given data:**

(i) $n_1 = 2$, $n_2 = 5$ (ii) $n_1 = 1$, $n_2 = 5$

Requirement:

$\bar{\upsilon} = ?$

Equation:

$$\bar{\upsilon} = 1.09678 \times 10^7\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]m^{-1}$$

Solution:

(i) $$\bar{\upsilon} = 1.09678 \times 10^7\left[\frac{1}{2^2}-\frac{1}{5^2}\right]m^{-1}$$

$$\bar{\upsilon} = 1.09678 \times 10^7\left[\frac{1}{4}-\frac{1}{25}\right]m^{-1}$$

$= 1.09678 \times 10^7 (0.21) m^{-1}$

$= 0.23 \times 10^7 \ m^{-1}$

$= 2.3 \times 10^6 \ m^{-1}$

Photon belong to Balmer series in visible region.

(ii) $$\bar{\upsilon} = 1.09678 \times 10^7\left[\frac{1}{1^2}-\frac{1}{25}\right]m^{-1}$$

$= 1.09678 \times 10^7 (0.96) m^{-1}$

$= 1.052 \times 10^7 \ m^{-1}$

Photon belongs to Lyman series in ultra violet region

(i) $2.3\times10^6 \ m^{-1}$ (visible region)

(ii) $1.052\times10^7 \ m^{-1}$ (U.V. region)

Q24. A photon of wave number $102.70 \times 10^5 \ m^{-1}$ is emitted when electron jumps from higher orbit to n = 1. Determine the number of higher orbit and series to which photon belongs.

Ans. **Given data:**

$n_1 = 1$, $\bar{v} = 102.70 \times 10^5 \ m^{-1}$

Rydberg constant = $1.09678 \times 10^7 \ m^{-1}$

Requirement:

$n_2 = ?$

Equation:

$$\bar{\upsilon} = 1.09678 \times 10^7\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]m^{-1}$$

Solution:

$$102.70 \times 10^5 \ m^{-1} = 1.09678 \times 10^7\left[\frac{1}{1^2}-\frac{1}{n_2^2}\right]m^{-1}$$

$$\frac{102.7\times10^5 m^{-1}}{1.09678\times10^7 m^{-1}} = 1-\frac{1}{n_2^2}$$

$$0.9363 = 1-\frac{1}{n_2^2}$$

$$\frac{1}{n_2^2} = 1-0.09363 = 0.0637$$

$$\sqrt{n_2^2} = \sqrt{15.708}$$

$n_2 = 3.96 \cong 4$ (Lyman series U.V. region)

Q25a. What is de Broglie's wavelength of an electron travelling at half a speed of light?

Ans. **Given data:**

Velocity of light = c = $3 \times 10^8 \ ms^{-1}$

Mass of electron = m = 9.1095×10^{-31} kg

Planck's constant = h = 6.625×10^{-34} Js

Requirement:

$\lambda = ?$

Equation:

$$\lambda = \frac{h}{mv}$$

Solution:

Half of velocity of light = $\frac{3\times10^8}{2} = 1.5\times10^8\, ms^{-1}$

$\lambda = \frac{6.625\times10^{-34}\, Js}{9.1095\times10^{-31}\, kg\times1.5\times10^8\, ms^{-1}}$ [J = kg m² s⁻²]

$\lambda = \frac{6.625\times10^{-34}\, kgm^2s^{-2}.s}{9.1095\times10^{-31}\, kg\times1.5\times10^8\, ms^{-1}} = 4.84\times10^{-12}\, m$

$= 0.484\times10^{-11}\, m = 0.0484\times10^{-10}\, m$ [$10^{-10}\, m = 1\, \mathring{A}$]

$= 0.0484\, \mathring{A}$

de Broglie's wavelength of electron = 0.0484 Å

Q25b. Convert the mass of electron into grams and velocity of light into cms^{-1} and then calculate the wavelength of the electron in cm.

Ans. **Given data:**

$c = 3\times10^8\, ms^{-1}$ [1 m = 10^2 cm]
$= 3\times10^{10}\, cms^{-1}$
$m = 9.1095\times10^{-31}\, kg$ [1 kg = 10^3 g]
$= 9.1095\times10^{-28}\, g$
$h = 6.625\times10^{-34}\, Js$ [1 J = 10^7 erg]
$= 6.625\times10^{-27}\, erg$ [1 erg = g cm² s⁻²]
$= 6.625\times10^{-27}\, g\, cm^2s^{-2}s$

Requirement:

λ in cm = ?

Equation:

$\lambda = \frac{h}{mv}$

Solution:

v = Half of velocity of light = $1.5\times10^{10}\, cms^{-1}$

So

$\lambda = \frac{6.625\times10^{-27}\, gcm^2s^{-2}s}{9.1095\times10^{-28}\, g\times1.5\times10^{10}\, gcms^{-1}} = 4.8\times10^{-10}\, cm$

$= 0.48\times10^{-9}\, cm = 0.048\times10^{-8}\, cm$

The Wavelength of an electron in cm = 0.048 × 10⁻⁸ cm

Q25c. Convert the wavelength of electron from meters to (i) nm (ii) Å (iii) pm.

Ans. **Given data:**

$\lambda = 0.048\times10^{-10}\, m$

Requirement:

λ in nm, Å, pm = ?

Relationship:

$10^{-10}\, m = 1\, \mathring{A}$
$10^{-12}\, m = 1\, pm$
$10^{-9}\, m = 1\, nm$

Solution:

(i) $0.048\times10^{-10}\, m$
$= 0.048\, \mathring{A}$ [$10^{-10}\, m = 1\, \mathring{A}$]

(ii) $0.048\times10^{-10}\, m$
$= 0.048\times10^{-9}\times10^{-1}\, m$ [$10^{-9}\, m = 1\, nm$]
So $0.048\times10^{-1}\, nm = 0.0048\, nm$

(iii) $0.048\times10^{-10}\, m = 4.8\times10^{-10}\times10^{-2}\, m$
$4.8\times10^{-12}\, m = 4.8\, pm$ [$10^{-12}\, m = 1\, pm$]

λ in m = $0.048\times10^{-10}\, m$
λ in cm = $0.048\times10^{-8}\, cm$
λ in Å = $0.048\, \mathring{A}$
λ in nm = 0.0048 nm
λ in pm = 4.8 pm

Additional Questions

Q. Bohr theory versus de Broglie equation.

Ans. One of the postulates of Bohr theory is that angular momentum of an electron is an integral multiple of $\frac{h}{2\pi}$

This postulate can be derived with the help of de Broglie concept of wave nature of electron.

So, $2\pi r = n\lambda$

or $\lambda = \frac{2\pi r}{n}$ .....(i)

From de Broglie equation,

$\lambda = \frac{h}{mv}$ .....(ii)

Thus, $\frac{h}{mv} = \frac{2\pi r}{n}$

or $mvr = n.\frac{h}{2\pi}$ (v = velocity of electron)
and r = (radius of the orbit)

i.e. Angular momentum $= n.\frac{h}{2\pi}$ ....(iii)

This proves that the de Broglie and Bohr concepts are in perfect agreement with each other.

Q. Bohr's theory is in well contradiction with Heisenberg's uncertainty principle. Justify it.

Ans. According to Bohr's theory an electron is material particle and is moving with specific velocity in orbits of specified radii. So its position as well as momentum can be determined with great accuracy. But according to uncertainty principle both these quantities cannot be measured experimentally.

Important Previous Board Questions

Q. How will you relate energy of emitted light with its frequency and wavelength?
Q. The energy associated with violet colour is greater than red colour in visible spectra. Why?
Q. What is the function of principal quantum number?
Q. Calculate ionization energy of hydrogen atom by using Bohr's Model.
Q. Give two defects of Rutherford's Atomic Model.
Q. Why the photographic plate is white and a few dark lines are there in the line absorption spectra of a substance?

For Answers study Scholar's CHEMISTRY (Objective) XI

Chapter 6

CHEMICAL BONDING

Chemical Bond

"The attractive force which holds together two or more atoms or ions to form a large variety of compounds is called a chemical bond."

Examples are ionic bond, covalent bond and coordinate covalent bond

The forces which are responsible for such bonding and the shapes of the molecules formed are as a result of chemical combination.

Cause of Chemical Combination

- It has been observed that the chemical reactivities of elements, depend upon their characteristic electronic configurations.
- The noble gases with electronic configuration of valence shells $1s^2$ (He) or $ns^2\ np^6$ (Ne, Ar, Kr, Xe and Rn) show little tendency to react chemically.
- Noble gases are the most stable of all the elements. Hence

(i) There are just only a few stable compounds, formed by these elements like XeF_2, XeF_4, $XeOF_2$, XeO_3 etc.

(ii) A noble gas does not react with another noble gas.

Why noble gases are most stable?

This can be explained on the basis of their special electronic configuration. Their outermost s and p-orbitals are completely filled.

Atoms of the Noble Gases are stable because all of their electrons are paired and the bonding shells are full.

$_2He$ = $\underset{1s}{\upharpoonleft\downharpoonright}$

$_{10}Ne$ = $\underset{1s}{\upharpoonleft\downharpoonright}\ \underset{2s}{\upharpoonleft\downharpoonright}\ \underset{2p_x}{\upharpoonleft\downharpoonright}\ \underset{2p_y}{\upharpoonleft\downharpoonright}\ \underset{2p_z}{\upharpoonleft\downharpoonright}$

In other words, noble gases obey octet and duplet rules which is the main cause of their stability and inertness.

Octet rule

"The tendency of atoms to attain a maximum of eight electrons in the valence shell is called 'octet rule'"

All other elements combine with one another, due to an inherent tendency to stabilize themselves. They get their stabilization by losing, gaining or sharing electrons to attain the nearest noble gas configuration

Change in electronic configuration of some elements after gaining or losing of electrons

Element	Tendency	Electronic Configuration		Nearest noble gas
		Before electron loss or gain	After electron loss or gain	
$_3Li$	Electron loss	$1s^2 2s^1$	$1s^2$	He (2)
$_{12}Mg$	Electron loss	$1s^2 2s^2 2p^6 3s^2$	$1s^2 2s^2 2p^6$	Ne (10)
$_9F$	Electron gain	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	$1s^2 2s^2 2p^6$	Ne (10)
$_{16}S$	Electron gain	$1s^2 2s^2 2p^6 3s^2 3p_x^2 2p_y^1 3p_z^1$	$1s^2 2s^2 2p^6 3s^2 3p^6$	Ar (18)

Important points about Octet rule

1. Noble gases have complete octets (He has complete duplet) and are chemically inert.
2. Inert gas configuration is attained by losing or gaining electrons under the octet rule.
3. In certain cases, both tendencies i.e. to lose or gain electrons have been observed. But the system will go by the conditions in which the chemical combination takes place.

For example, in the chemical combination between sodium and hydrogen to form **NaH**, hydrogen atom gains an electron. In the formation of **HF**, hydrogen atom donates the major share of its electron to fluorine atom.

Q. Which of the species given below violates the octet rule?
(a) CF_4 (c) BF_3
~~(c) N_2O~~ (d) NO_2

LIMITATIONS OF THE OCTET RULE

The octet rule , though useful is , is not universal. It is quite useful , for understanding the structures of most organic compounds and it applies mainly to the second period elements of periodic table. There are three types of exceptions to the octet rule

The incomplete octet of the central atom:

In some compounds , the number of electrons surrounding the central atom is less than eight. This is specially the case with elements having less than four valence electrons. Examples are LiCl, BeH_2 and BCl_3

Li : Cl H : Be : H Cl : B(Cl) : Cl

Li, Be and B have 1, 2 and 3 valence electrons only. Other such compounds are $AlCl_3$ and BF_3.

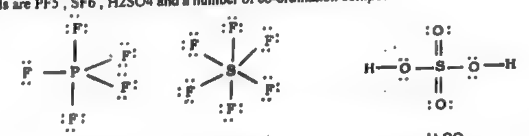
Odd Electron molecules:

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxideNO_2 , the octet rule is not satisfied for all atoms.

N = O O = N — O

The expanded octet :

Elements in and beyond the third period of the periodic table have apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obiously the octet rule does not apply in such cases. Some examples of such compounds are PF5 , SF6 , H2SO4 and a number of co-ordination compounds.



PF_5 SF_6 H_2SO_4

Sulphur also forms many compounds in which the octet rule is obeyed. In sulphur chloride the S atom has an octet of electrons around it.

: Cl — S — Cl : or : Cl : S : Cl :

ENERGETICS OF BOND FORMATION

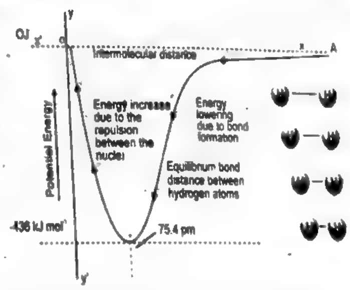
According to the modern theory of chemical bonding, atoms form bonds as it leads to a decrease in energy. Since low energy state is stable state so in molecular form, they get stability.

Example: Formation of H_2 molecule

When two hydrogen atoms approach each other, forces of attraction and repulsion operate simultaneously.

- **The attractive forces** tend to bring the two atoms close to each other and the potential energy of the system is decreased.
- On the other hand, **repulsive forces** tend to push the atoms apart and potential energy of the system is increased.

It has been found that the magnitude of potential energy for attractive forces is more than for repulsive forces. Therefore, potential energy decreases as the two hydrogen atoms approach each other.



Bond distance / Compromise distance / Bond length

Eventually, a state corresponding to the distance of 75.4pm is reached, where

(i) Attractive forces dominate the repulsive forces.
(ii) Potential energy of the system is minimum.
(iii) Hydrogen atoms bonded to form a stable molecule.

So, this distance of 75.4pm is called bond distance or bond length or compromise distance of two hydrogen atoms.

Bond energy

When the atoms approach the distance of minimum energy, then the system of two hydrogen atoms is stabilized to maximum extent. The amount of energy evolved is 436.45kJmol^{-1} and is called bond formation energy. In order to break the bond, the same amount of energy has to be provided which is called bond dissociation energy.

$$H + H \rightarrow H_2 \qquad \Delta H = -436.45\ kJmol^{-1}$$
$$H_2 \rightarrow H + H \qquad \Delta H = +436.45\ kJmol^{-1}$$

Consequences of dominant repulsion forces

When repulsive forces are dominant than the attractive forces then:

(i) Energy of the system increases.
(ii) It leads to instability.
(iii) A chemical bond is not formed.

ATOMIC SIZES

The size of an atom is very important because many physical and chemical properties are related to it. Atoms are assumed to be spherical. That is why, we report the various types of radii to guess their sizes. For this reason, the sizes of atoms are expressed in terms of atomic radii, ionic radii and covalent radii, etc. depending upon the type of the compound used for its measurement.

Atomic Radii

"The average distance between the nucleus of an atom and its outermost electronic shell is called **atomic radius**."

- Atomic radii can be determined by measuring the distances between the centres of adjacent atoms with the help of X-rays or spectroscopic measurements.
- The units for atomic radius are pm, nm or Å .

Why the radius of an atom cannot be determined precisely

The atomic radius cannot be determined precisely due to the following reasons:

(i) There is **no sharp boundary** of an atom. The probability of finding an electron never becomes exactly zero even at a large distance from the nucleus.
(ii) The **electronic probability distribution** is affected by neighbouring atoms. For this reason, the size of an atom may change from one compound to another.

Periodic Trend

Across the period

Atomic radii decrease from left to right across the period. It is due to.

(i) Increase in nuclear charge

(ii) Shielding effect remains almost same across the period.

As the nuclear charge increases, the pull on the electrons is increased and size of an atom decreases.

The decrease of atomic radii is very prominent in second period, but less in higher periods. Moreover, the decrease is small, when we travel from left to right in transition elements Sc(21) – Zn(30), Y(39) – Cd(48) due to the intervening electrons

Shielding Effect/Screening Effect

"The decrease in attraction of nucleus and valence **electrons** due to presence of **intervening electrons** is called shielding effect or screening effect."

This is responsible for the decrease in force of attraction of the nuclous for the electrons present in the valence shell

- It remains almost constant across the period.
- It increases down the group due to increase in number of intervening electrons.

Down the group

Atomic radii increase down the group due to

(i) increase in number of shells

(ii) increase in the shielding effect

Ionic Radii

"The radius of an ion while considering it to be spherical in shape is called ionic radius."

Q. Why the size of a cation is smaller than its parent atom?

Cationic Radius

A cation is formed by the loss of electron or electrons from a neutral atom.

The ionic radius of a cation is smaller than the atomic radius of the element from which it is derived. It is due to

(i) Imbalance of electron-proton ratio.

(ii) Nucleus holds the remaining electrons with a stronger force.

(iii) Usually there is loss of shell occurs during removal of electron.

Consequently radius of cation is smaller than its parent atom.

Q. The species that has the same number of electrons as $^{35}_{17}Cl^-$ is

(a) $^{35}_{17}Cl^+$ (c) $^{32}_{16}S^+$

(c) $^{40}_{18}Ar^+$ (d) $^{35}_{16}S^{2-}$

For Example

$$\underset{186\ pm}{Na} \longrightarrow \underset{95\ pm}{Na^+} + 1e^-$$

Q. Why the size of anion is greater than its parent atom?

Anionic radius

An anion is formed by the gain of electron or electrons by a neutral atom.

The ionic radius of an anion is greater than the atomic radius of the corresponding atom. It is due to:

(i) Imbalance of electron-proton ratio.

(ii) Nucleus holds the remaining electrons with a weaker force.

(iii) During the addition of electrons, electronic cloud expands and anionic radii increases.

For Example

$$\underset{99\ pm}{Cl} + 1e^- \longrightarrow \underset{181\ pm}{Cl^-}$$

It should be kept in mind that ionic radius for metals is for positive ions and for elements of group number VA to VIIA are for negative ions.

Periodic Trend

The ionic radii decrease from left to right in a period and increase from top to bottom in a group. The cationic radius decreases with the increase in the effective nuclear charge on the ion. The decrease in radius is larger for divalent ions (Mg^{2+}) and still larger for trivalent ions (Al^{3+}).

Variation of ionic radii in isoelectronic ions

Atomic radius (pm)		Ionic radius(pm)	
Cl	99	Cl^-	181
Br	114	Br^-	195
I	133	I^-	216
O	73	O^{2-}	140
S	102	S^{2-}	184
N	75	N^{3-}	171

Radii of iso-electronic ions

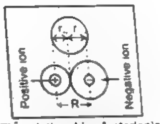
Ion	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}
Number of electrons	10	10	10	10	10
Charge on the nucleus	+7	+8	+9	+11	+12
Radius (pm)	171	140	136	95	60

Relationship of interionic distance R and ionic radii

Let us consider, the positive and negative ions, which are held together by electrostatic forces of attraction in a crystal lattice. r_+ and r_- are the values of radii of cation and anion, respectively.

The interionic distance 'R' in a crystal lattice is equal to the sum of the cationic radius r_+ and the anionic radius r_-

$$R = r_+ + r_-$$



The relationship of interionic distance R and ionic radii

Pauling was able to determine the distance between K^+ and Cl^- ions in potassium chloride crystal and found that it was equal to the sum of the radii of the two ions.

$$R = 133pm + 181pm = 314pm$$

Thus, the ionic radius appeared to be an additive property. Pauling extended this concept to other K^+ salts and calculated the radii of other ions from the relationship:

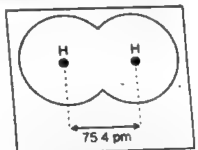
$$r_- = R - r_+$$

Similarly, the ionic radii of different cations can also be determined.

Covalent Radii

"The covalent radius of an element is defined as half of the single bond length between two similar atoms covalently bonded in a molecule."

For example, The covalent radius of H_2 is 37.7 pm and it is half of the single bond length (75.4 pm) between the two H – atoms in H – H molecule .



Covalent radius of H atom, (75.4/2 = 37.7 pm)

Determination of covalent radii

The covalent radius of an atom can be used to determine the covalent radius of another atom. For example, the experimentally determined bond length of C – Cl in CH_3Cl is 176.7 pm. The covalent radius of Cl-atom being known as 99.4 pm, that of C-atom can be calculated by subtracting this value from C-Cl bond length. So, the covalent radius of C-atom = 176.7 – 99.4 = 77.3 pm.

Periodic trend

The covalent radii decrease from left to right in a period and increase from top to bottom in a group.

Q.5 Define ionization energy. How it change in periodic table what factors are responsible for its variations?

Ionization Energy

"The minimum amount of energy required to remove an electron from the valence shell of an isolated gaseous atom to form a cation is called **ionization energy**."

For examples

$H \longrightarrow H^+ + 1e^-$ $\quad \Delta H = +1313\ kJ\ mol^{-1}$

$Li \longrightarrow Li^+ + 1e^-$ $\quad \Delta H = +520\ kJ\ mol^{-1}$

$Na \longrightarrow Na^+ + 1e^-$ $\quad \Delta H = +496\ kJ\ mol^{-1}$

$Mg \longrightarrow Mg^+ + 1e^-$ $\quad \Delta H = +738\ kJ\ mol^{-1}$

$$\text{I.E} \propto \text{stability} \propto \frac{1}{\text{Reactivity}}$$

- Ionization energy is actually the qualitative measure of the stability of an isolated atom. Greater the ionization energy more stable will be the atom.
- It is measured in $kJ\ mol^{-1}$, $k\ cal\ mol^{-1}$ or eV
- Noble gases have highest ionization energy values and thus they have high stability and least reactivity.

Factors Influencing the Ionization Energy

Ionization energies of atoms depend upon:

(i) Atomic Radius of Atom

As the atomic radius decreases, valence shell comes close to the nucleus.

$$\text{I.E} \propto \frac{1}{\text{atomic radius}}$$

(ii) Nuclear Charge

Greater the nuclear charge, greater will be the ionization energy.

$$\text{I.E} \propto \text{Nuclear charge}$$

(iii) Shielding Effect of inner electrons

Greater the shielding effect, lesser will be the ionization energy.

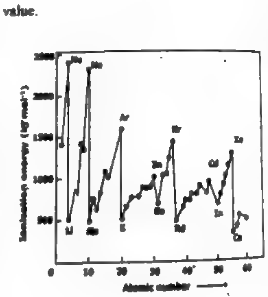
$$\text{I.E} \propto \frac{1}{\text{Shielding effect}}$$

(iv) Penetration Effect

Arrangement of orbitals according to increasing ionization energy value.

$$s > p > d > f$$

Variation of Ionization Energy in the Periodic Table



Across the period

In the periodic table, the ionization energy increases from left to right in a period due to:

(i) Increase in the proton number, until a maximum value is reached at the end of the period. This may be explained in terms of the periodicity of the electronic configuration of elements. Each period begins with an element which has one electron in its valence shell and ends with the completion of an electronic shell.

(ii) The increase in the atomic number is associated with the increase in nuclear charge which leads to a stronger force of attraction between the nucleus and the increasing number of electrons. The stronger force of attraction, ultimately results in difficult removal of electrons.

(iii) Decrease in atomic radius.

Down the group

The ionization energy decreases in the group due to:

(i) Successive addition of electronic shells as a result of which the valence electrons are placed at a larger distance from the nucleus. As the force of attraction between the nucleus and the outer electron decreases with the increase in distance, the electron can be removed more easily or with less energy.

(ii) The force of attraction also decreases due to increasing shielding effect of the intervening electrons which causes decrease in ionization energy.

Abnormalities of ionization energy values in periods

There are following abnormalities:

(i) The ionization energy values of IIIA group elements are less as compared to IIA.

Reason

In IIIA group, electron is being removed from the p-subshell which is more extended orbital than s orbital. Moreover, we have to break the pairs from s-orbitals of IIA group elements. Due to this reason, II-A group elements show abnormally high I.E values.

(ii) The elements of VA group have high ionization energy values than VIA group elements

Reason

In V-A group, elements have half-filled p-subshell. This half-filled p-subshell is extra stable. This extra stability associated with nitrogen family enhances their I.E values. In this way, VIA group elements have abnormal ionization energies.

$$_7N = 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$$

$$_8O = 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$$

Q. Which of the following 2nd period element has highest ionization energy value?
(a) B (b) N (c) C (d) O

Higher Ionization Energies

Second Ionization energy

"The amount of energy required to remove the second electron after removal of first electron to form a di-positive ion is called second ionization energy."

Example

$Mg^+ \longrightarrow Mg^{2+} + 1e^-$ $\quad \Delta H = +1450\ kJ\ mol^{-1}$

Third Ionization energy

"The amount of energy required to remove the third electron from outermost shell after the removal of second electron is called third **ionization energy**."

Example

$Mg^{2+} \longrightarrow Mg^{3+} + 1e^-$ $\quad \Delta H = +7730\ kJ\ mol^{-1}$

It is clear from ionization energy values that

Third I.E > Second I.E > First I.E

Q. Second I.E value is always higher than first I.E value. Justify

Ans. This is due to reason that second electron is removed from a positively charged ion rather than a neutral atom. The dominant positive charge holds the electrons more tightly and thus further removal of electrons becomes more difficult.

$Mg \longrightarrow Mg^+ + e^-$ $\quad \Delta H = 738\ kJ\ mol^{-1}$

$Mg^+ \longrightarrow Mg^{++} + e$ $\quad \Delta H = 1450\ kJ\ mol^{-1}$

Applications of Ionization Energy

(i) Index to metallic character

Ionization energy is an index to metallic character. The elements which have

(i) Low ionization energies are **metals.**

(ii) High ionization energies are **non-metals.**

(iii) Intermediate ionization energies are **metalloids.**

(ii) Ionization energy and Valency of an element

The gaps in the first, second, third and higher ionization energies help us to guess the valency of an element. If, there is sufficient gap between first ionization energy and second one, then the element shows valency of one. **For example,** carbon has six electrons and has six I.E values. The reasonable gap of I.E is present between fourth and fifth. That is why carbon has valency four.

(iii) Reactivity of metals

The reactivity of metals is inversely proportional to ionization energy. Metals will low ionization energy (IA group) are highly reactive and vice versa.

Q.5 Define Electron Affinity. How it is change in periodic table. What factors are responsible for its variations?

Electron Affinity

"The energy released when an electron adds to an empty or partially filled orbital of an isolated gaseous atom in its valence energy level to form an anion having a unit negative charge is called electron affinity."

Examples

$$Cl_{(g)} + 1e^{-1} \rightarrow Cl^{-1}_{(g)} \qquad \Delta H = -349\,kJ\,mol^{-1}$$

$$F_{(g)} + 1e^{-1} \rightarrow F^{-1}_{(g)} \qquad \Delta H = -322\,kJ\,mol^{-1}$$

Since, energy is released, so electron affinity is given the negative sign. Electron affinity is the measure of the **attraction of the nucleus of an atom for the extra electron.**

Factors affecting electron affinity

Following factors affect electron affinity:

(i) Atomic radius ⟶ E.A $\propto$ 1/atomic radius
(ii) Nuclear charge ⟶ E.A $\propto$ nuclear charge
(iii) Shielding effect ⟶ E.A $\propto$ 1/shielding effect

Units: Its units are kJ mol^{-1}, k cal mol^{-1}, electron volt.

Variation in the periodic table

Across the Period

In a period, the atomic radius decreases due to increase in the nuclear charge. Thus, the electron affinities of elements increase from left to right in the periodic table. That is why, the alkali metals have the lowest and the halogens have the highest electron affinities.

Down the group

In groups, the atomic radii increase with the increase in the proton number due to successive increase of electronic shells. This also exerts a shielding effect on the force of attraction between the nucleus and the valence electrons. Thus, the electron affinities usually decrease from top to bottom.

Abnormal behaviour of electron affinities in periods

- The elements of **IIA group** i.e., Be, Mg, Ca etc. have two electrons in the s-orbital. They don't accommodate the incoming electrons. Their electron affinities are less than IA group elements. So in every period of the period table, IIA group elements show abnormal behaviour.
- Elements of **VA group** i.e. N, P, As etc. have half-filled p-subshells which is extra stable. Hence in every period, these elements show electron affinity values lower than IVA.
- Noble gases (VIIIA) have complete outermost shell and their electron affinities are zero.

Q. Electron affinity of fluorine is less than chlorine although electron affinity values decrease down the group. Justify it.

Ans. Actually fluorine has very small size (72 pm) and seven electrons in 2s and 2p subshells have thick electronic cloud. This thick electronic cloud repels the incoming electron. Thus fluorine have electron affinity less than that of chlorine.

$$Cl_{(g)} + 1e^{-1} \rightarrow Cl^{-1}_{(g)} \qquad \Delta H = -349\,kJ\,mol^{-1}$$

$$F_{(g)} + 1e^{-1} \rightarrow F^{-1}_{(g)} \qquad \Delta H = -322\,kJ\,mol^{-1}$$

Q. Why the second value of electron affinity of an element is usually shown with a positive sign?

Ans. Usually the electronegative elements release energy when first electron is added into them. But when a second electron is added in a uni-negative ion, the incoming electron is repelled by the already present –ive ion (charge). In order to overcome this repulsion, energy is absorbed during the process. Thus the formation of a di-negative ion is an endothermic process and its E.A. is shown with positive sign.

$$O + e^- \rightarrow O^- \qquad E.A_1 = -141\,kJ\,mol^{-1}$$

$$O^- + e^- \rightarrow O^{-2} \qquad E.A_2 = +780\,kJ\,mol^{-1}$$

Q. Explain what do you understand by the term electronegativity? Discuss its variations in the periodic table. How does it affect the bond strengths?

Electronegativity

"The tendency of an atom to attract a shared electron pair towards itself in a molecule is called electronegativity."

- It has no unit.

Explanation

For a homonuclear diatomic molecule e.g. H_2, the bonding pair of electrons is equally shared between the atoms. On the other hand, in a bond between dissimilar atoms such as in HF, the electron density of the bonding electrons lies more towards the fluorine atom than towards the hydrogen atom. This unequal sharing is due to fact that F-atom has greater tendency than H-atom to attract shared electron pair between them. It is related to the ionization energy and the electron affinity of the element.

Q. Which of the following is not a thermodynamic property of an element?
(a) Ionization energy
(b) Electron affinity
(c) Electronegativity
(d) None of these

Measurement of electronegativity Pauling scale

Pauling calculated the electronegativity values of elements from the difference between the expected bond energies for their normal covalent bond and the experimentally determined values.

He devised an electronegativity scale on which **fluorine** is given an arbitrary standard value **4.0** (Highest E.N value) and the electronegativity value of **cesium is 0.7** (Lowest E.N value). The electronegativity values of **other elements** are compared with fluorine.

Variation of Electronegativities in Periodic Table

Electronegativity difference	% Ionic character
0.1	0.5
0.2	1
0.6	10
1.1	25
1.7	50
2.3	75
3	90

Across the period

Electronegativity increases from left to right in the period due to:

(i) Decrease in atomic size
(ii) Shielding effect remains constant

Down the group

Electronegativity decreases down the group due to:

(i) Increase in atomic size
(ii) Shielding effect increases

Application of electronegativity

1. Nature of chemical bond

The difference in the electronegativity values of the bonded atoms is an index to the nature of chemical bond.

(i) When the electronegativity difference is zero, the bond between the two atoms is non-polar covalent bond.
(ii) Those bonds which are formed between different elements are mostly polar e.g. HCl, CCl_4 etc.
(iii) Elements of widely different electronegativities form ionic bonds e.g. NaCl, MgO, KBr etc.
(iv) A difference of 1.7 units shows roughly equal contributions of ionic and covalent bonds.

2. Bond Strength

Greater the electronegativity difference between bonded atoms, greater will be the bond strength and vice versa.

TYPES OF BONDS

Chemical bonds can be classified as:

(i) Ionic bond
(ii) Covalent bond
(iii) Coordinate covalent bond

We shall explain these bonds with the help of different theories of chemical bonding. First of all let us discuss the Lewis concept of bond formation.

LEWIS CONCEPT

With the help of this concept, we can understand the tendencies of elements to have relation with each other.

Ionic Bond or Electrovalent Bond

"The electrostatic force of attraction between oppositely charged ions i.e. cation and anion is called ionic bond or electrovalent bond."

Formation of Ionic-bond

- According to **Lewis theory**, ionic bond is formed by the complete transfer of electron or electrons from an atom with low ionization energy to another atom with high electron affinity.
- In energy terms, the electropositive elements (metals) are at a higher energy state than the electronegative elements (non-metals). The energy difference will be responsible for the transfer of electrons from a higher energy state to a lower energy state.
- If the electronegativity difference is more than 1.7 between two bonded atoms then ionic bond will be formed.

IA group form ionic bond with VIIA

IA	VIIA
Li^+	F^{-1}
Na^+	Cl^{-1}
K^+	Br^{-1}
Rb^+	I^{-1}

IIA group form ionic bond with VIA

IIA	VIA
Be^{+2}	O^{-2}
Mg^{+2}	S^{-2}
Ca^{+2}	Se^{-2}
Sr^{+2}	Te^{-2}

1. Formation of Potassium Chloride

Let us consider the formation of potassium chloride.

(i) The electronic configuration of potassium is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$. It may be represented as K(2, 8, 8, 1). It tends to lose the outermost electron to form K^+ ion. The energy needed to detach the electron from potassium atom is equal to its first ionization energy. So

$$K_{(2,8,8,1)} \longrightarrow K^+_{(2,8,8)} + 1e^- \qquad \Delta H = 419.0 \text{ kJ mol}^{-1}$$

After the loss of an electron, potassium attains the nearest inert gas configuration of Ar(2, 8, 8)

(ii) The electronic configuration of chlorine is $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ or Cl(2, 8, 7). It tends to gain electron, lost from potassium atom, to attain nearest inert gas configuration of Ar(2, 8, 8) releasing 348.6 kJ mol^{-1} energy which corresponds to electron affinity of chlorine.

$$Cl(2, 8, 7) + 1e^{-1} \longrightarrow Cl^{-1}(2, 8, 8) \qquad \Delta H = -349 \text{ kJ mol}^{-1}$$

(iii) The oppositely charged K^+ and Cl^- ions are held together by strong **electrostatic force of attraction**.

(iv) K^+ and Cl^- ions arrange themselves to form a crystal lattice where proportionate number of cations and anions are packed together. The energy released during the formation of crystal lattice is **690 kJ mol^{-1}**. It is called lattice energy of KCl.

$$K^+ + Cl^- \longrightarrow KCl \qquad \Delta H = -690 \text{ kJ mol}^{-1}$$

2. Formation of CaO

Calcium oxide contain ions in the ratio of $Ca^{2+} : O^{2-}$.

$$Ca(2, 8, 8, 2) \longrightarrow Ca^{2+}(2, 8, 8) + 2e^-$$
$$O(2, 6) + 2e^- \longrightarrow O^{2-}(2, 8)$$
$$Ca^{2+} + O^{2-} \longrightarrow CaO$$

3. Formation of Al_2O_3

Al^{3+} and O^{2-} ions are present in ratio 2 : 3.

$$Al(2, 8, 3) \longrightarrow Al^{3+}(2, 8) + 3e^-$$
$$O(2, 6) + 2e^- \longrightarrow O^{2-}(2, 8)$$
$$3O^{2-} + 2Al^{3+} \longrightarrow Al_2O_3$$

Similarly, CaS and Al_2S_3 are also ionic compounds to some extent.

Ionic Compounds/Electrovalent Compounds

"The compounds formed by cations and anions are called ionic or electrovalent compounds."

Examples are KCl, CaO, CaS, Al_2O_3, Al_2S_3 etc.

- There exist a strong electrostatic force of attraction between cations and anions in these compounds

% Age of ionic nature in a compound

Criteria of electronegativity also help us to understand nature of bond. So, in order to decide the % of ionic nature in a compound, it is better to note the difference of electronegativity between the bonded atoms. If the difference is 1.7 or more than that, then the bond is said to be ionic. e.g. NaCl has 72% ionic character and CaF has 92% ionic character.

Q. No bond in chemistry is 100% ionic in nature. Why?

Ans. During ionic bond formation, when a cation approaches an anion, the net positive charge on cation tends to

(i) attract electrons of anions.

(ii) repel nucleus of anions.

Combined effect of these two forces results in distortion of electronic cloud of anion. Anion is **polarized** and cation has **polarization power**.

Anion also has same effect but not to a prominent extent due to small cationic size.

Due to polarization of ions, a covalent character (mutual sharing of electrons) is observed in ionic compounds. So no bond in chemistry is 100% ionic. e.g., strongest ionic bond is present in CsF ($\Delta EN = 3.2$) with 92% ionic character.

Covalent Bond (Electron Pair Bond)

"The force of attraction between shared electrons pair and nucleus of bonded atoms is called **covalent bond**."

Formation

- According to Lewis and Kossel, a covalent bond is formed by mutual sharing of electrons between two atoms. While sharing, each atom completes its valence shell and attains nearest inert gas configuration.
- If electronegative difference between bonded atoms is less than 1.7, then bond formed is covalent.

Types of Covalent Bond (On the basis of polarity)

There are two types of covalent bond:

1. Non-polar covalent bond.
2. Polar covalent bond.

(i) Non-polar Covalent Bonds

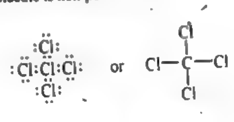
- In such bonds, electronegativity difference is less than 0.4.
- The bonding electrons pair is equally shared.
- Due to even distribution of charge, the bonded atoms remain electrically neutral.

Examples

Hydrogen	Chlorine
H : H or H—H	:Cl:Cl: or Cl—Cl

The other molecules are F_2, Br_2, I_2 etc.

- CCl_4 is a non-polar covalent bond. This is due to cancellation of all dipoles of this molecule due to its symmetry Actually, all the C-Cl are polar but molecule is non-polar overall.
- **Tetrachloromethane**



- Covalent and ionic compounds are bonded differently and they behave differently. You cannot apply 'ionic bonding ideas' to a compound that is covalent.
- Ionic bonds are present in a compound of a metal and non-metal.
- Covalent bonds are present in a compound of two non-metals.

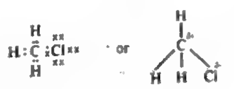
- The molecules like CH_4, SiH_4 and $SiCl_4$ also follow same attitude of non-polarity due to symmetry of structure.

(2) Polar Covalent Bonds

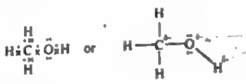
- If the electronegativity difference between the bonded atoms is more than 0.4 upto 1.7, then bond is polar covalent bond.
- When two different atoms are joined by a covalent bond, the electrons pair is not equally shared between bonded atoms.
- The bonding pair of electrons will be displaced towards more electronegative atom. This would make one end of molecule partially positive and other partially negative.

Examples

Methyl chloride



Methanol



An atom can share more than one electrons.

Nitrogen

N_2 is an inert gas having a strong triple bond.

: N : : : N : or : N≡N:

The molecule of O_2 makes a double bond.

Oxygen

O : : O or O = O

Carbon dioxide is a non-polar covalent compound, although it is formed from heteroatoms. The linear structure balances the polar character on both sides of the carbon atom.

Carbon dioxide

: O : : C : : O : or O = C = O

Some of non-metallic atoms, particularly carbon atoms mutually share their electrons with each other. This leads to formation of extended chains which is basis for formation of large sized molecules called **macromolecules**. For examples, diamond, graphite, SiC etc.

Types of Covalent Bond (On the basis of numbers)

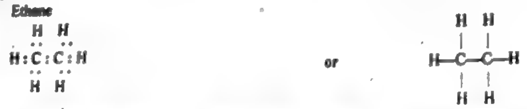
1. Single covalent bond
2. Double covalent bond
3. Triple covalent bond

Single covalent bond

A bond formed by mutual sharing of one electrons pair is called single covalent bond. It is represented by (—).

Example

Ethane

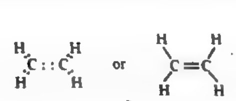


Double covalent bond

A bond formed by mutual sharing of two electrons pairs is called double covalent bond. It is represented by (=).

Example

Ethene



Triple covalent bond

A bond formed by mutual sharing of three electrons pairs is called triple covalent bond. It is represented by (≡).

Example

Ethyne

H : C : : C : H or H − C ≡ C − H

Q7. Which of the following molecules will be polar or non-polar. Sketch the structure and justify your answer.
(i) CCl_4 (ii) SO_3 (iii) SF_4 (iv) NF_3 (v) PF_3 (vi) SO_2 (vii) SF_6 (viii) IF_7

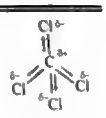
Ans. (i) CCl_4:

Shape: Regular tetrahedral

$\mu = 0$

Reason: All vectors created by individual bonds are cancelled so a net polar effect is zero.

Result: Non - polar molecule



$\mu = 0$

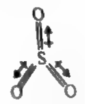
(ii) SO_3:

Shape: Triangular planar

μ: zero

Reason: All dipoles of SO_3 are cancelled due to its symmetry

Result: Non - polar molecule



$\mu = 0$

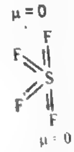
(iii) SF_4:

Shape: Seasaw like instead of trigonal bipyramidal

$\mu > 0$

Reason: Distortion of structure due to lone pair. A net effect of bond-vectors is observed.

Result: Polar molecule



$\mu = 0$

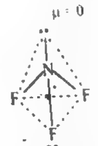
(iv) NF_3:

Shape: Pyramidal

$\mu > 0$

Reason: Distortion of structure due to lone pair. A net effect of bond vectors is observed.

Result: Polar molecule



(v) PF_3:

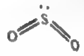
Shape: pyramidal.

$\mu > 0$

Reason: Direction of structure due to lone pair. A net effect of bond vectors is observed.

Result: Polar molecule

(vi) SO_2:



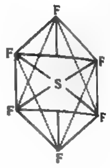
Shape: Angular

$\mu > 0$

Reason: Structure is distorted due to lone pair so bond vectors have a net effect.

Result: Polar molecule

(vii) SF_6:



Shape: Octahedral (regular)

$\mu = 0$

Reason: Bond vectors cancel the effect of each other due to regular structure.

Result: Non polar

(viii) IF_7:

Shape: Regular pentagonal bipyramidal.

$\mu = 0$

Reason: Bond vectors cancel the effect of each other.

Result: Non - polar molecule

Q. Describe polar and non–polar molecules?

Ans. (i) Polar and non-polar molecules:

Molecules charges on bonded atoms have partial positive and partial negative centres because of difference of electronegativity. Additional attractive force is created between bonded atoms due to dipole formation. As a result bond is stronger than it is expected

Example:-

Bond energy (Calculated) for H–Cl = 336 kJ/mol^{-1}

Bond energy (observed) for H–Cl = 432 kJ/mol^{-1}

Difference in Bond energy = Bond energy (observed) – Bond energy (calculated) = 432 – 336 = 96 kJ mol^{-1}

Difference in Bond energy is created due to extra strength of polar bond/ionic character of molecule.

On the other hand, no dipole formation occurs in non-polar molecule, so bond is comparatively weaker e.g., bond energy of Cl–Cl = 242 kJ mol^{-1}.

Hence, we conclude that a polar bond is stronger than non-polar bond due to ionic character present in it.

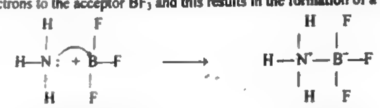
Coordinate Covalent Bond (Dative bond)

"The bond between two atoms when the shared pair of electrons is donated by one of the bonded atoms is called coordinate covalent bond."

Examples

(i) The bond formation between NH_3 and BF_3.

NH_3 has three covalent bonds and there is a lone pair of electrons on nitrogen atom. On the other hand, boron atom in BF_3 is deficient in a lone pair of electrons. Actually, the octet of B is not complete in BF_3. Therefore, nitrogen can donate the pair of electrons to the acceptor BF_3 and this results in the formation of a coordinate covalent bond.

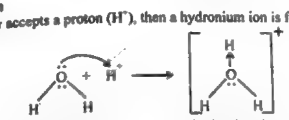


donor acceptor complex

- After formation of a coordinate covalent bond, the distinction between covalent and coordinate covalent bond vanishes.

(ii) Hydronium ion

When water accepts a proton (H^+), then a hydronium ion is formed.

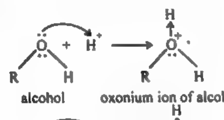


donor acceptor hydronium ion

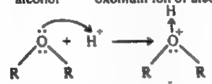
- All the three bonds between oxygen and hydrogen have equal status.
- Every bond is 33% coordinate covalent and 66% covalent.

(iii) Oxonium ion

All the alcohols and ethers offer their lone pairs to H^+ just like water to form coordinate covalent bonds. The ions so produced are called oxonium ions.



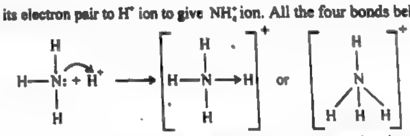
alcohol oxonium ion of alcohols



an ether oxonium ion of ethers

(iv) Ammonium ion

Ammonia donates its electron pair to H^+ ion to give NH_4^+ ion. All the four bonds behave alike, in NH_4^+ ion.

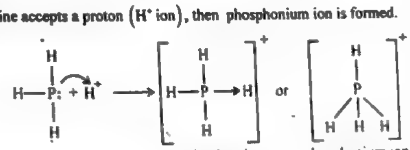


ammonium ion ammonium ion

All the primary, secondary and tertiary amines like ammonia make such bonds with H^+ ion.

(v) Phosphonium ion

When PH_3, phosphine accepts a proton (H^+ ion), then phosphonium ion is formed.



phosphonium ion phosphonium ion

- Coordinate covalent bonds are present in HNO_3.
- Many oxyacids of halogens like ($HClO_2$, $HClO_3$, $HClO_4$) have coordinate covalent bonds between chlorine and oxygen.

Limitations of Lewis Concept

Classical Lewis model can successfully explain:

1. How atoms are bonded to one another to form a molecule.
2. How the electrons are shared between the bonded atoms.

But Lewis model does not explain the **shapes and geometries of molecules**. Since shapes of molecules are very important for explaining many physical and chemical properties of substances.

So Lewis model has no wide acceptance in Chemistry.

Write down the necessary features for a true model of covalent bond formation

(i) A true model should be able to justify molecular shapes and geometries of molecules, bond polarities, bond distances and various energy transitions as evident by spectroscopic techniques.

(ii) This model should also make clear the unique behavioural features of molecules during chemical reactions.

Q6. Write the Lewis structures for the following compounds:

(i) HCN (ii) CCl_4 (iii) CS_2 (iv) $H_3N \longrightarrow AlF_3$ (v) NH_4OH
(vi) H_2SO_4 (vii) H_3PO_4 (viii) $K_2Cr_2O_7$ (ix) N_2O_5 (x) $Ag(NH_3)_2NO_3$

Ans.

(i) HCN

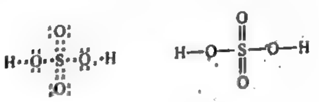
(ii) CCl_4

(iii) CS_2

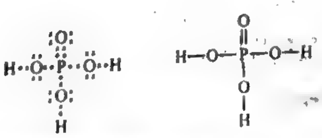
(iv) $H_3N \longrightarrow AlF_3$

(v) NH_4OH

(vi) H_2SO_4



(vii) H_3PO_4



(viii) $K_2Cr_2O_7$

(ix) N_2O_5

(x) $[Ag(NH_3)_2]NO_3$

MODERN THEORIES OF COVALENT BOND

Following are the modern theories, which explain satisfactorily the above requirements for covalent bond formation, based on wave mechanical structure of atoms.

1. Valence shell electron pair repulsion theory (VSEPR Theory)
2. Valence bond theory (VBT)
3. Molecular orbital theory (MOT)

In addition to above, crystal field theory and ligand field theory explain the formation of coordination complex compounds formed by transition metals.

VSEPR Theory

VSEPR stands for "**valence shell electron pairs repulsion theory**"

Introduction

1. Sidgwick and Powell

Sidgwick and Powell in 1940 pointed out that the shapes of molecules could be interpreted in terms of electron pairs in the outermost orbit of the central atom.

2. Nyholm and Gillespie

Nyholm and Gillespie developed VSEPR theory, which explains the shapes of molecules for non-transition elements.

Basic assumptions

The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsions at a minimum.

Postulates of VSEPR theory

(i) Both the lone pairs as well as bond pairs participate in determining the geometry of the molecules.

(ii) The electron pairs are arranged around the central polyvalent atom so as to remain at a maximum distance apart to avoid repulsions.

(iii) The electron pairs of lone pairs occupy more space than the bond pairs.

A bonding electron pair is attracted by both nuclei of atoms while non-bonding by only one nucleus. Because a lone pair experiences less nuclear attraction, its electronic charge is spread out more in space than that for bonding pair. As a result, the non-bonding electron pairs exert greater repulsive forces on bonding electron pairs and thus tend to compress the bond pairs.

The magnitude of repulsions between electron pairs in a given molecule decreases in following order:

Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

These repulsions are called **van der Waals repulsions.**

(iv) The two electron pairs of double bond and three electron pairs of a triple bond, contain a higher electronic charge density. Therefore, they occupy more space than one electron pair of a single bond but behave like single electron pair in determining the geometry of the molecules. This is because, they tend to occupy the same region between the two nuclei like a single bond.

Shapes of molecules according to VSEPR theory

In order to illustrate the VSEPR theory, let us consider that the central atom is 'A' and it is a polyvalent atom. Number of side atoms depends upon valency (combining power) of central atom. More than one 'B' type atoms are linked with 'A' to give different type of molecules like.

1. AB_2 type molecules
2. AB_3 type molecules
3. AB_4 type molecules

1. Molecules Containing Two Electron Pairs (AB_2 type)

Number of electron pairs

Two electron pairs.

Bonding pairs

Two bonding pairs.

Lone pair

No lone pair.

Arrangement of electron pairs

Linear

Molecular geometry

Linear.

Shape

180°
B ×·A·× B
OR
180°
B—A—B

- Central atom or polyvalent atom is from group IIA or IIB.
- Side atoms may be from VIIA.

Molecule	Electron pairs			Type	Arrangement of pairs	Molecular geometry	Shape
	T	Bonding	Lone				
$BeCl_2$	2	2	0	AB_2	Linear	Linear	180° Cl—Be—Cl
$MgCl_2$	2	2	0	AB_2	Linear	Linear	180° Cl—Mg—Cl

$CaCl_2$, $SrCl_2$, $CdCl_2$ and $HgCl_2$ are also linear molecules.

2. Molecules Containing Three Electron Pairs (AB_3 type)

(a) AB_3 Type with No Lone Pairs

Number of electron pairs

Three electron pairs.

Bonding pairs

Three bonding pairs.

Lone pair

No lone pair.

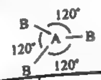
Arrangement of electron pairs

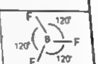
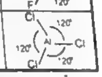
Trigonal planer.

Molecular geometry

Trigonal planar.

Shape



Molecule	Electron pair			Type	Arrangement of pairs	Molecular geometry	Shape
	T	Bonded	Lone				
BF_3	3	3	0	AB_3	Trigonal	Trigonal planar	
$AlCl_3$	3	3	0	AB_3	Trigonal	Trigonal planar	

We expect similar geometries in hydrides of group III-A (AlH_3, GaH_3, InH_3 and TlH_3) and their halides

(b) AB_3 Type with One Lone Pair and Two Bond Pairs

Total electron pairs

Three electron pairs.

Bonding pairs

Two bonded pairs.

Lone pairs

One lone pair.

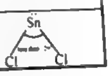
Arrangement of electron pairs

Triangular planar.

Molecular geometry

Bent or angular.

Shape

Molecule	Electron pairs			Type	Arrangement	Geometry	Shape
	T	B	L				
$SnCl_2$ [Stanous chloride]	3	2	1	AB_3	Triangular planar	Bent or angular	

Examples

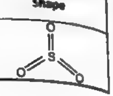
$SnCl_2$ has AB_3 type molecule with one lone pair. In $SnCl_2$ one of the corner of the triangle is occupied by a lone pair, giving rise to a distorted triangular structure in vapour phase.

(c) AB_3 Type with Multiple Bonds

In SO_2, one corner of triangle is occupied by a lone pair and two corners each by S = O double, bond.

Molecule	Electron pairs			Type	Arrangement	Geometry	Shape
	T	B	L				
SO_2 [Sulphur dioxide]	3	2	1	AB_3 with multiple bonds	Triangular planar	Bent or angular	

In SO_3, all three regions, each are occupied by S = O bonds. This structure of SO_3 is perfectly triangular.

Molecule	Electron pairs			Type	Arrangement	Geometry	Shape
	T	B	L				
SO_3 [Sulphur trioxide]	3	3	0	AB_3 with multiple bond	Triangular planar	Triangular planar	

3. Molecules Containing Four Electron Pairs (AB_4 Type)

(a) AB_4 Type with no Lone Pairs

Molecules containing four electron pairs.

Total electron pairs

Four electron pairs

Bonding pairs

Four bonding pairs.

Lone pair

No lone pair.

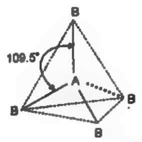
Arrangement of electron pairs

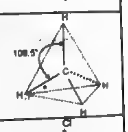
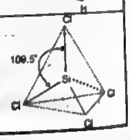
Tetrahedral.

Molecular geometry

Tetrahedral.

Shape



Molecule	Electron pairs			Type	Arrangement of pairs	Geometry	Shape
	T	B	L				
CH_4	4	4	0	AB_4	Tetrahedral	Tetrahedral	
$SiCl_4$	4	4	0	AB_4	Tetrahedral	Tetrahedral	

On the same grounds, SiH_4, GeH_4, CCl_4 form similar geometries. This structure has four corners, four faces, six edges and six bond angles.

(b) AB_4 Type with One Lone Pair and Three Bond Pairs

Total electron pairs

Four electron pairs.

Bonding pairs

Three bonding pairs.

Lone pair

One lone pair.

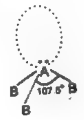
Arrangement of electrons pairs

Tetrahedral

Molecular geometry

Trigonal pyramidal.

Shape

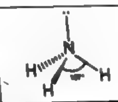


Example

Ammonia, NH_3 is a typical example.

$_7N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

The non-bonding electron in 2s orbital takes up more space and exerts a strong repulsive force on the bonding electron pairs. Consequently, to avoid a larger repulsion, the bonding electron pairs move closer that reduces the ideal bond angle from 109.5° to 107.5°. This effect compels ammonia to assume a triangular pyramidal geometry instead of tetrahedral, as in methane.

Molecules	Electron pairs			Type	Arrangement of pairs	Geometry	Shape
	T	B	L				
NH_3 Ammonia	4	3	1	AB_4	Tetrahedral	Trigonal Pyramidal	

Similar affects are evident in the geometries of molecules like PH_3, AsH_3, SbH_3 and BiH_3.

Q. Bond angle in $\ddot{N}F_3$ (102°) is less than in $\ddot{N}H_3$ (107.5°). Justify.

Ans. In NF_3, the strong polarity of N-F bond pulls the lone pair of N atom closer to its nucleus, which in turn exerts a stronger repulsion over bonding electrons. Thus, the angle further shrinks to 102°. Moreover, the bond pairs in N-F bonds are more close to F atoms than N atoms. The increased distances in these bond pairs make their repulsions less operative.

(c) AB_4 Type with Two Lone Pair and Two Bond Pairs

Total electron pairs

Four electron pairs.

Bonding pairs

Two bonding pairs.

Lone pairs

Two lone pairs.

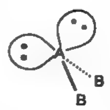
Arrangement of the electron pairs

Tetrahedral.

Molecular geometry

Bent or angular.

Shape

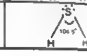


For example: Water (H_2O), a triatomic molecule is expected to be an AB_2 type linear molecule like $BeCl_2$ and CO_2. But, experimental evidences confirm a bent or angular geometry. VSEPR theory, successfully justifies the experimental results by arguing the participation of lone pairs, in addition to bond pairs in determining overall geometry of water molecule.

$${}_8O = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$$

Two of the corners of a tetrahedron are occupied by each of the two lone pairs and remaining by bond pairs. But owing to spatial arrangement of lone pairs and their repulsive action among themselves and on bond pairs, the bond angle is further reduced to 104.5°.

H_2S, H_2Se, H_2Te form similar geometries.

Molecule	Electron pairs			Type	Arrangement of pairs	Geometry	Shape
	T	B	L				
H_2O	4	2	2	AB_4	Tetrahedral	Bent or angular	
H_2S	4	2	2	AB_4	Tetrahedral	Bent or angular	

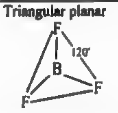
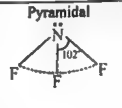
Limitations of VSEPR theory

VSEPR theory predicts and explains the shapes of molecules but does not give reasons for the formation of bonds. VBT is concerned with both the formation of bonds and the shapes of molecules.

Q9. The molecules of NF_3 and BF_3 have same molecular formula of the XF_3 type. But they possess different structural formulas. Keeping in view VSEPR theory, sketch the shape of each molecule and explain origin of differing in shapes.

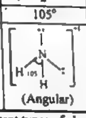
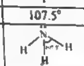
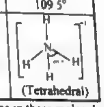
Ans. According to VSEPR theory shapes of molecules are mainly based on number of electron pairs and their arrangement around the central atom. Nitrogen and Boron are central atoms of these compounds belonging to V-A and III-A groups respectively.

According to VSEPR, they can be explained as follows:

	BF_3	NF_3
Type of molecules	AB_3	AB_4
No. of bond pairs	3	3
No. of lone pairs	0	1
Bond angle	120°	102°
Shapes of molecules	Triangular planar 	Pyramidal 

Q10. The species NH_2^-, NH_3, NH_4^+ have bond angles of 105°, 107.5° and 109.5° respectively. Justify these values by drawing their structures.

Ans. We can explain these molecules on the basis of VSEPR theory

	NH_2^-	NH_3	NH_4^+
Type of molecules	AB_4	AB_4	AB_4
No of bond pairs	2	3	4
No. of lone pairs	2	1	0
Bond angles	105°	107.5°	109.5°
Shapes of molecules	 (Angular)	 (Pyramidal)	 (Tetrahedral)

Difference in bond angle is due to different types of electronic repulsions in these molecules

(i) In NH_4^+, due to presence of all four bond pairs, magnitude of repulsions is same. Therefore, structure is regular tetrahedral with an angle of 109.5°.

(ii) In NH_3, presence of one lone pair distorts the geometry of molecule, as lone pair-bond pair repulsions are greater than bond pair-bond pair repulsions causing a decrease in angle i.e., 107.5°.

(iii) In NH_2^- due to two lone pairs, greatest repulsions of lone pair-lone pair distorts the structure to a greater extent and bond angle decreases to 105°.

Valence Bond Theory (VBT)

According to valence bond theory, the partially filled atomic orbitals overlap to form bonds but the individual characters of atomic orbitals are retained. Greater the overlap, the stronger will be the bond formed.

Introduction

It was introduced by Hitler and London in 1927. Later on, it was further extended by Pauling. It is based on quantum mechanical principle and gives us information about

(i) Shapes of molecules.
(ii) Bond formation in molecules.

Explanation

According to quantum mechanical approach, a covalent bond is formed when half filled orbitals in outer or valence shells of two atoms overlap, so that a pair of electrons, one electron from each atom, occupies the overlapped orbital. As a result of their overlap, the electrons with opposite spins become paired to stabilize themselves. Larger the overlap, stronger is the bond. The essential conditions for chemical bonding are:

1. The orbitals of atoms participating in the bond formation must overlap.
2. The direction of bond is determined by the direction of two overlapping orbitals.

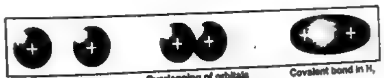
Types of bonds

There are two types of bonds:

(i) Sigma bond (σ - bond)
(ii) Pi – bond (π-bond)

Examples: (1) Formation of H_2 Molecule

$H = 1s^1$



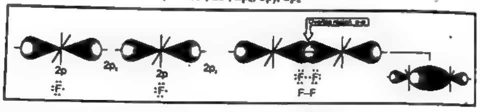
s and s orbital overlap in H_2

- As the two hydrogen atoms approach each other, their 1st orbitals overlap.
- They give H-H bond. The electron density becomes concentrated between the two nuclei. The bond is called σ bond (sigma bond).

(2) Formation of F_2 Molecule

The bond in the fluorine molecule (F_2) is formed by the overlap of half-filled $2p_z$ orbital on each fluorine atom.

$$_9F = 1s^2, 2s^2, 2p_x^{\uparrow\downarrow}, 2p_y^{\uparrow\downarrow}, 2p_z^{\uparrow}$$



The formation of the fluorine molecule

(3) Formation of HF Molecule

The H-F bond is formed by the pairing of electrons – one from hydrogen and one from fluorine. According to VB theory, we must have two half-filled orbitals – one from each atom that can be joined by overlap.

$$_1H = 1s^{\uparrow} \qquad _9F = 1s^2, 2s^2, 2p_x^{\uparrow\downarrow}, 2p_y^{\uparrow\downarrow}, 2p_z^{\uparrow}$$

The overlap of orbitals provides a means for sharing electrons, thereby allowing each atom to complete its valence shell. The fluorine atom completes its 2p subshell by acquiring a share of an electron from hydrogen as shown below.

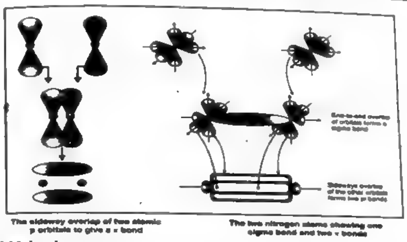
$$HF = 2s^{\uparrow\downarrow}, 2p_x^{\uparrow\downarrow}, 2p_y^{\uparrow\downarrow}, 2p_z^{\uparrow\downarrow}$$

The requirements for bond formation are met by overlapping the half–filled 1s orbital of hydrogen with the half-filled 2p orbital of fluorine. There are then two orbitals plus two electrons whose spins can adjust so they are paired. The formation of the bond is illustrated in Fig.

The formation of the hydrogen fluoride molecule

(4) Formation of Nitrogen (N_2) Molecule

Consider, the bonding between nitrogen atoms having the electronic configuration $_7N = 1s^2, 2s^2, 2p_x^{1}, 2p_y^{1}, 2p_z^{1}$. The three unpaired electrons on each atom are located in perpendicular p-orbitals, which are oriented so that if one end-to-end p-orbital overlap occurs (resulting in a sigma bond), the other two p-orbitals cannot overlap in the same fashion. Rather, they are aligned parallel to the corresponding orbital in the other atom.



The sideway overlap of two atomic p orbitals to give a π bond

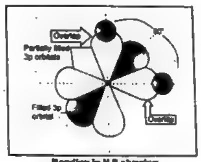
The two nitrogen atoms showing one sigma bond and two π bonds

(5) Formation of H_2S Molecule

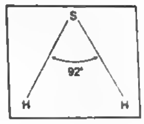
H_2S is a non-linear molecule, and the bond angle between the two H-S bonds is about 92°. Each two 3p-orbitals of sulphur containing one electron can overlap with the 1s orbitals of hydrogen atoms.

$$_{16}S = 3s^{\uparrow\downarrow}, 3p_x^{\uparrow\downarrow}, 3p_y^{\uparrow}, 3p_z^{\uparrow}$$

$$H_2S = 3s^{\uparrow\downarrow}, 3p_x^{\uparrow\downarrow}, 3p_y^{\uparrow\downarrow}, 3p_z^{\uparrow\downarrow}$$



Bonding in H_2S showing overlap of orbitals



Thus, the VBT requires the idea of overlap to explain the geometry of the hydrogen sulphide molecule.

Q. A sigma (σ) bond is stronger than a pi (π) bond. Justify.

Ans: σ bond is formed by linear overlap of atomic orbitals and charge density is concentrated between two nuclei so greater forces of attraction are present here.

On the other hand, π bond is formed by parallel overlapping of orbitals and charge density lies above and below the line joining the two nuclei. As a result a comparatively less force of attraction is present here.

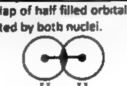
So σ bond is stronger than a π bond.

For example:

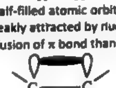
C–C bond is σ in nature.
Bond energy of C–C = 348 kJ mol^{-1}
C = C has one σ and one π bond.
Bond energy of C = C = 614 kJ mol^{-1}
Difference between two bond energies is (614 – 348) = 266 KJ mol^{-1}
Which is bond energy of π bond.
Bond energy of π bond < Bond energy of σ-bond.

Q.18. (iv) π bonds are more diffused than σ bond.

Sigma bond is formed by the linear overlap of half filled orbitals. In σ bond, electronic charge density lies along the inter-nuclear axis and strongly attracted by both nuclei.



π bond is formed by parallel overlap of half-filled atomic orbitals. In π bond electronic charge density lies above and below the inter-nuclear axis and is weakly attracted by nuclei.
Less nuclear attraction causes a more diffusion of π bond than σ-bond.



Q. Differentiate between σ and π bond.

Difference between σ and π bond

Sr. #	Sigma bond (σ)	Pi bond (π)
(i)	Sigma bond is formed by linear or head to head overlapping of partially filled orbitals.	Pi bond is formed by parallel or side to side overlap of atomic orbitals.
(ii)	Representation of sigma bond is 'σ'.	Representation of Pi bonds is π.
(iii)	Electronic charge density is present on bond axis between the two nuclei.	Electronic charge density is present above and below bond axis of two nuclei.
(iv)	Charge density of σ-bond is comparatively less diffused than π and due to stronger nuclear attraction.	Charge density of π bond is more diffused due to lesser nuclear attraction.
(v)	Sigma bond is stronger.	π bond is weaker.
(vi)	σ-bond is comparatively inert.	π bond is comparatively reactive.
(vii)	Bonded atoms always form σ-bond firstly and then π-bond if necessary.	π-bond formation is preceded by σ-bond formation.
(viii)	Examples: $\underset{\sigma\text{-bond}}{H–H}$	$O\underset{\pi}{\overset{\sigma}{=}}O$

Limitations of VBT

Following are the limitations of VBT:

1. It fails to explain the paramagnetic behaviour of oxygen.
2. VBT does not explain the equivalent tetravelency of carbon in methane.
3. It fails to tell the bond angle in water and ammonia.

Atomic Orbital Hybridization

"The process in which mixing of atomic orbitals having different shapes and energies to form hybrid orbitals with same shape and energy but different orientation is called hybridization."

- According to this, the atomic orbitals differing in shapes and energies intermix to form new orbitals which are called **hybrid orbitals**.
- They differ with the parent atomic orbitals in shape and possess specific geometry.

Explanation

- The atomic orbital hybridization gives us a satisfactory explanation for the valency of the elements.
- The electrons belonging to ground state are promoted to the excited state as a result of which there is an increase in the number of unpaired electrons.
- These excited orbitals undergo hybridization simultaneously because the promotion of electrons and hybridization is a simultaneous process.
- The energy required for excitation is compensated by the energy released during hybridization and the process of bond formation with other atoms.
- Hybridization leads to entirely new shape and orientation of valence orbitals of atom.
- It holds significant importance in determining the shape and geometry of molecules.

Types of hybridization

Depending upon the number and nature of the orbitals participating in hybridization, different types of hybridization take place which are as follows:

1. sp^3 hybridization
2. sp^2 hybridization
3. sp hybridization

i) sp^3 HYBRIDIZATION

"In sp^3 hybridization, one s and three p atomic orbitals (slightly differ in energy) intermix to form four equivalent orbitals called sp^3 hybrid atomic orbitals."

i) Bonding and Structure of Methane (CH_4)

Electronic Configuration of Carbon

Ground state electronic configuration of carbon is:

$${}_6C \text{ (ground state)} = \overset{\uparrow\downarrow}{1s},\ \overset{\uparrow\downarrow}{2s},\ \overset{\uparrow}{2p_x},\ \overset{\uparrow}{2p_y},\ 2p_z$$

Hybridization occurs only in central atom. Therefore, we consider carbon during hybridization.
Excited state electronic configuration of carbon is:

$${}_6C \text{ (excited state)} = \overset{\uparrow\downarrow}{1s},\ \overset{\uparrow}{2s},\ \overset{\uparrow}{2p_x},\ \overset{\uparrow}{2p_y},\ \overset{\uparrow}{2p_z}$$

All these atomic orbitals have different shapes and energies.

Formation of hybrid orbitals

Four half filled atomic orbitals of carbon intermix to form four hybrid orbitals.

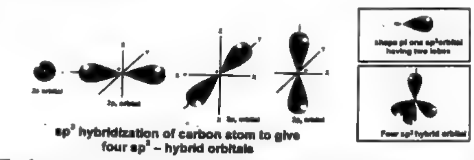
$${}_6C \text{ (hybridized state)} = \overset{\uparrow\downarrow}{1s},\ \overset{\uparrow}{sp^3},\ \overset{\uparrow}{sp^3},\ \overset{\uparrow}{sp^3},\ \overset{\uparrow}{sp^3}$$

All these hybrid orbitals have

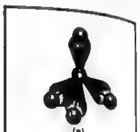
(i) Same shapes.
(ii) Same energies (degenerate orbitals).
(iii) Different orientation in space.
(iv) More stable than atomic orbitals.

Orientation of hybrid orbitals

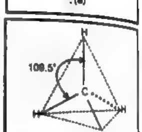
As hybrid orbitals have different orientations in space. Each sp^3-hybrid orbital consists of two lobes, one large and other smaller



sp^3 hybridization of carbon atom to give four sp^3 – hybrid orbitals



(a)



(b)

Four sp^3-s overlaps in tetrahedral structure of CH_4 molecule

The four equivalent hybrid orbitals are directed towards the four corners of a regular tetrahedron. They are oriented in space in such a manner that the angle between them is 109.5°

Formation of methane molecule

Methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms separately to form four sigma bonds. The molecule thus formed, possesses a **tetrahedral** geometry. The four C-H bonds which result from **sp^3-s overlaps** are directed towards the corners of a regular tetrahedron. The tetrahedral structure of CH_4 has four faces, four corners, six edges and six bond angles of 109.5°.

(ii) Bonding and Structure of Ammonia (NH_3)

Electronic Configuration of Nitrogen

Ground state electronic configuration of nitrogen is:

$$_7N \text{ (ground state)} = \overset{\uparrow\downarrow}{1s}, \overset{\uparrow\downarrow}{2s}, \overset{\uparrow}{2p_x}, \overset{\uparrow}{2p_y}, \overset{\uparrow}{2p_z}$$

All these atomic orbitals have different **shapes and energies**.

Formation of hybrid orbitals

Four atomic orbitals of nitrogen intermix to form four **hybrid orbitals**.

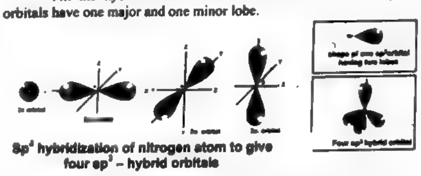
$$_7N \text{ (hybridized state)} = \overset{\uparrow\downarrow}{sp^3}, \overset{\uparrow}{sp^3}, \overset{\uparrow}{sp^3}, \overset{\uparrow}{sp^3}$$

All these hybrid orbitals have:

(i) Same shapes
(ii) Same energies
(iii) Different space orientations
(iv) More stable than atomic orbitals

Orientation of hybrid orbitals

All the hybrid orbitals have different orientations in space. Each sp^3-hybrid orbitals have one major and one minor lobe.

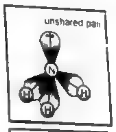


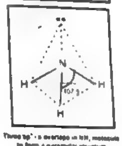
Sp^3 hybridization of nitrogen atom to give four sp^3 – hybrid orbitals

These all are directed towards the four corners of a tetrahedron.

Formation of ammonia molecule

The nitrogen atom undergoes **three sp^3-s overlaps** with three s-orbitals of hydrogen atoms. The three hydrogen atoms are located at the three corners whereas the lone pair of electrons is at the fourth corner of tetrahedron. The result is a **pyramidal molecule** in which the three hydrogen atoms forms the base and the lone pair of electrons forms the apex.





Three sp^3-s overlaps in NH_3 molecule to form a pyramidal structure

Q. Why the bond angle in NH_3 (107.5°) is less than tetrahedral angle (109.5°)

Ans. The experimentally determined angle in NH_3 is 107.5°. The deviation from the tetrahedral angle 109.5° is explained on the basis of repulsion between the lone pair and the bond pair of electrons. The lone pair is closer to the nucleus of nitrogen than the bond pair and thus bond angle in ammonia is decreased.

(iii) Bonding and Structure of Water (H_2O)

Electronic configuration of oxygen

$$_8O \text{ (ground state)} = \overset{\uparrow\downarrow}{1s}, \overset{\uparrow\downarrow}{2s}, \overset{\uparrow\downarrow}{2p_x}, \overset{\uparrow}{2p_y}, \overset{\uparrow}{2p_z}$$

These atomic orbitals have different shapes and energies.

Formation of hybrid orbitals

Here 2s and three 2p-orbitals of oxygen intermix to form four sp^3-hybrid orbitals.

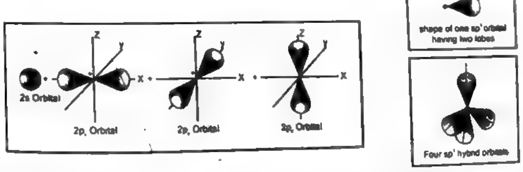
$$_8O \text{ (hybridized state)} = \overset{\uparrow\downarrow}{sp^3}, \overset{\uparrow\downarrow}{sp^3}, \overset{\uparrow}{sp^3}, \overset{\uparrow}{sp^3}$$

These hybrid orbitals have:

(i) Same shapes.
(ii) Same energies.
(iii) Different orientations in space.
(iv) More stable than atomic orbitals.

Orientation of hybrid orbitals

All the hybrid orbitals have different orientations in space. Each sp^3 – orbital has one major and one minor lobe



Formation of water molecule

Two hybrid orbitals are completely filled by the two available lone pairs of electrons. The remaining two half-filled orbitals undergo **sp^3-s overlaps** with hydrogen atoms to form sigma bonds. The two H-atoms occupy two corners of the tetrahedron and the remaining two corners are occupied by two lone pairs of electrons. Water molecule has bent or angular structure.

Shape

sp^3 - s overlaps in H_2O to form an angular structure

Q. Water has bent or angular structure rather than tetrahedral. Justify.

Ans. The bond angle in H_2O is $104.5°$. The deviation from the tetrahedral angle $(109.5°)$ is explained on the basis of repulsion between the two lone pairs of electrons with bond pairs. The lone pairs are closer to the nucleus of oxygen. They repel bond pairs and the bond angle decreases from $(109.5°)$ to $(104.5°)$. So, the molecule of water has bent or angular structure.

(2) sp^2-HYBRIDIZATION

"In sp^2 hybridization, one s and two p-atomic orbitals (slightly differ in energy) intermix to form three equivalent orbitals called sp^2 hybrid atomic orbitals."

1. Bonding and structure of boron tri-fluoride (BF_3)

Electronic configuration of Boron

The ground state electronic configuration of central atom boron is:

$_5B$ (ground state) = $\overset{\uparrow\downarrow}{1s}, \overset{\uparrow\downarrow}{2s}, \overset{\uparrow}{2p_x}, 2p_y, 2p_z$

All the atomic orbitals have different shapes and energies. The excited state electronic configuration of Boron is:

$_5B$ (excited state) = $\overset{\uparrow\downarrow}{1s}, \overset{\uparrow}{2s}, \overset{\uparrow}{2p_x}, \overset{\uparrow}{2p_y}, 2p_z$

Formation of hybrid orbitals

One s and two p-atomic orbitals of an atom intermix to form three hybrid orbital called sp^2-hybrid orbitals.

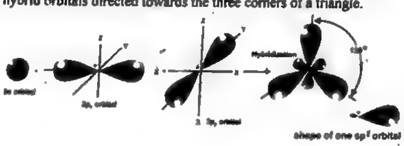
$_5B$ (hybridzed state) = $\overset{\uparrow}{sp^2}, \overset{\uparrow}{sp^2}, \overset{\uparrow}{sp^2}, 2p_z$

These hybrid orbitals have:

(i) Same shapes
(ii) Same energies
(iii) Different orientations in space
(iv) More stable than atomic orbitals

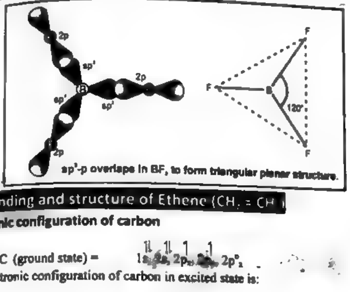
Orientation of hybrid orbitals

The hybrid orbitals have different orientations in space. Each sp^2-hybrid orbital consists of two lobes one major and one minor. These are hybrid orbitals directed towards the three corners of a triangle.



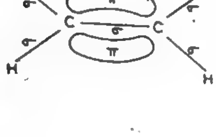
Formation of BF_3 Molecule

One of the p-orbitals of fluorine is half filled i.e. $2p_z$. This p-orbital of F is in the form of a lobe BF_3 is formed by the overlap of three half-filled sp^2 hybrid orbitals of boron with lobe shaped p-orbitals of three fluorine atoms. The structure is triangular planer.



sp^2-p overlaps in BF_3 to form triangular planar structure.

(b) Bonding and structure of Ethene ($CH_2 = CH_2$)



Electronic configuration of carbon

$_6C$ (ground state) = $\overset{\uparrow\downarrow}{1s}, \overset{\uparrow\downarrow}{2s}, \overset{\uparrow}{2p_x}, \overset{\uparrow}{2p_y}, 2p^0_z$

The electronic configuration of carbon in excited state is:

$_6C$ (exciteed state) = $\overset{\uparrow\downarrow}{1s}, \overset{\uparrow}{2s}, \overset{\uparrow}{2p_x}, \overset{\uparrow}{2p_y}, \overset{\uparrow}{2p_z}$

$_6C$ (hybridized state) = $\overset{\uparrow}{sp^2}, \overset{\uparrow}{sp^2}, \overset{\uparrow}{sp^2}, \overset{\uparrow}{2p_z}$

Formation of ethene molecule

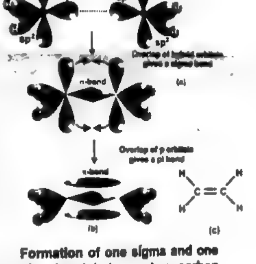
In the formation of ethene molecule, each carbon atom undergoes sp^2 hybridization to form three hybrid orbitals which are co-planar and are oriented at an angle of $120°$. Each atom is left with one half filled p-orbital perpendiculars to the planar sp^2 hybrid orbital. One of the p-orbitals does not take part in hybridization. Each carbon atom undergoes sp^2-s overlaps with two hydrogen atoms and sp^2- sp^2 overlap between themselves to form sigma bonds.

π-bondformation

The partially filled p-orbitals undergo sideways overlap to form a π – bond. So, a π – bond is formed by the sideways overlap of two half-filled co-planar p-orbitals in such a way that the probability of finding the electron is maximum perpendicular to the line joining the two nuclei. It should be made clear that a π – bond is formed between two atoms only when they are already bonded with a sigma bond.

Molecular geometry

The two clouds of the π – bond are perpendicular to the plane in which five σ – bonds are lying. Just like σ – bond, π – bond can be represented by a line.



Formation of one sigma and one pi – bond between two carbon atoms in C_2H_4

(3) sp-HYBRIDIZATION

"In sp hybridization, one s and one p-atomic orbitals (slightly differ in energy) intermix to form two equivalent orbitals called sp hybrid atomic orbitals."

(a) Bonding and structure of beryllium dichloride ($BeCl_2$)

Electronic configuration of beryllium

The electronic configuration of central atom (Be) in ground state is

$${}_4Be\ \text{(ground state)} = \overset{\uparrow\downarrow}{1s}, \overset{\uparrow\downarrow}{2s}, 2p_x, 2p_y, 2p_z$$

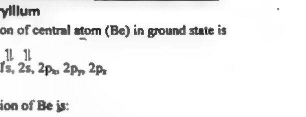
Excited state electronic configuration of Be is:

$${}_4Be\ \text{(excited state)} = \overset{\uparrow\downarrow}{1s}, \overset{\uparrow}{2s}, \overset{\uparrow}{2p_x}, 2p_y, 2p_z$$

$${}_4Be\ \text{(hybridized state)} = \overset{\uparrow}{sp}, \overset{\uparrow}{sp}$$

Formation of Be Cl_2 molecule

The two sp hybrid orbitals lie in linear way. $BeCl_2$ is formed when two sp hybrid orbitals of Be atom overlap with the half-filled p-orbitals of chlorine atoms. The outermost half-filled $3p_z$ orbital of Cl has lobe shape.



Molecular geometry

Be atom lies at the center and two Cl atoms on either side so that the Cl-Be-Cl angle is 180°.

$$Cl - \overset{180^\circ}{Be} - Cl$$

(b) Bonding and structure of Ethyne (HC≡CH)

Electronic configuration of carbon

The electronic configuration of carbon in ground state is:

$${}_6C\ \text{(ground state)} = \overset{\uparrow\downarrow}{1s}, \overset{\uparrow\downarrow}{2s}, \overset{\uparrow}{2p_x}, \overset{\uparrow}{2p_y}, 2p_z$$

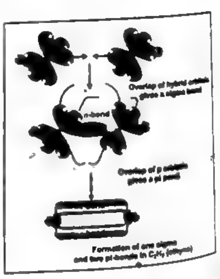
The electronic configuration in excited state is:

$${}_6C\ \text{(excited state)} = \overset{\uparrow\downarrow}{1s}, \overset{\uparrow}{2s}, \overset{\uparrow}{2p_x}, \overset{\uparrow}{2p_y}, \overset{\uparrow}{2p_z}$$

$${}_6C\ \text{(hybridized state)} = \overset{\uparrow}{sp}, \overset{\uparrow}{sp}, \underbrace{\overset{\uparrow}{2p_y}, \overset{\uparrow}{2p_z}}_{\text{Unhybrid}}$$

Formation of ethyne molecule

Ethyne is formed as a result of sp-hybridization of carbon atoms and subsequent formation of σ and π bonds. Each carbon atom undergoes **sp-s overlap** with one hydrogen atom and **sp-sp overlap** with other carbon atom. Each carbon atomis left with two unhybridized p orbitals perpendicular to the plane of sp hybrid orbitals. The two half-filled p-orbitals (on separate carbon atoms) are parallel to each other in one plane while the other two p orbitals are parallel to each other in another plane. The sideways π overlap between the p-orbitals in two planes results in the formation of two π bonds.



Formation of one sigma and two pi-bonds in C_2H_2 (ethyne)

Molecular geometry

Ethyne molecule contains one σ and two π bonds between the two carbon atoms and each carbon atom is bonded with one H atom through a σ bond. Actually, four electronic clouds of two π-bonds intermix and they surround the sigma bond in the shape of a drum.

$$H - \overset{180^\circ}{C} \equiv C - H$$

SUMMARY

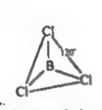
	No. of hybrid-orbitals	No. of non-hybrid orbitals in case of carbon	Molecular geometry	s-character	p-character
sp^3	4	0	tetrahedral	25%	75%
sp^2	3	1	triangular	33%	66%
sp	2	2	linear	50%	50%

Q11. (b) The linear geometry of $BeCl_2$ suggests that central atom Be is sp-hybridized. What type of hybridization is observed when atoms attached to central atom are located at the corner of (a) an equilateral triangle (b) a regular tetrahedron and (c) triangular bipyramide?

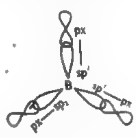
Ans. (a) An equilateral triangle:

If central atom undergoes sp^2 hybridization then resultant three orbitals are arranged at the corners of an equilateral triangle with an angle of 120°.

Example: BCl_3



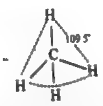
Equilateral triangle



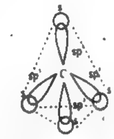
(b) A regular tetrahedron:

If one s and 3p orbitals intermix they give rise to four hybrid sp^3 orbitals arranged at corners of regular tetrahedral with a bond angle of 109.5°.

Example: CH_4



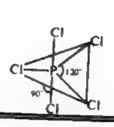
Regular tetrahedral

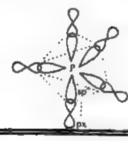


(c) Triangular bipyramide:

If one s, three p and one d orbitals of central atom undergo hybridization, they give rise to form sp^3d hybrid orbitals located at the corners of triangular bipyramide.

Example: PCl_5

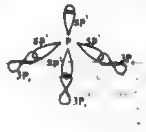




Q13. (b) Sketch the hybrid orbitals of PCl_3, SF_6, $SiCl_4$ and NH_4^+

Ans. **PCl_3:**

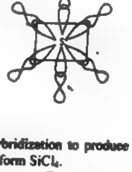
In PCl_3 'P' is sp^3 hybridized. Four sp^3 hybrid orbitals are arranged at the corner of tetrahedron. Three sp^3 hybrid orbitals of 'P' overlap with $3p_x$ orbital of Cl to form three sigma bonds.



Pyramidal structure

SF_6:

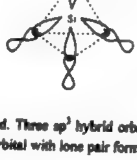
In SF_6 'S' is d^2sp^3 hybridized to give six hybrid orbital arranged octahedrally. Each hybrid orbital of 'S' overlap with $2p_z$ orbital of F to form six sigma bonds.

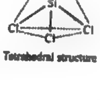


Octahedral structure

$SiCl_4$:

In $SiCl_4$ 'Si' undergoes sp^3 hybridization to produce four sp^3 hybrid orbitals arranged tetrahedrally. Each has linear overlap with $3p_z$ of Cl to form $SiCl_4$.

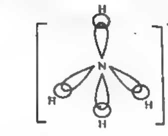


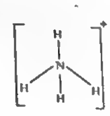


Tetrahedral structure

NH_4^+:

In NH_4^+ 'N' is sp^3 hybridized. Three sp^3 hybrid orbitals have linear overlap with 1s orbitals of three hydrogen atoms while one sp^3 hybrid orbital with lone pair form coordinate covalent bond with H^+.





Q13. (a) Sketch the molecular orbital pictures of

(i) $\pi(2p_y)$ and $\pi^*(2p_y)$ (ii) O_2, O_2^{+1}, O_2^{-1} (iii) He_2, Ne_2

Molecular Orbital Theory

This theory was proposed by Hund and Mulliken in 1932. The molecular orbital approach considers the whole molecule as a single unit. According to molecular orbital theory:

- The atomic orbitals of the combining atoms overlap to form new orbitals called molecular orbitals (MOs) which are characteristic of the whole molecule.
- The molecular orbital surrounds two or more nuclei of the bonded atoms.
- Two atomic orbitals, after overlapping, form two molecular orbitals which differ in energy
- One of them, having lower energy, is called bonding molecular orbital (B.M.O) while the other having higher energy is called anti-bonding molecular orbital (A.B.M.O).
- The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (molecular axis). It is designated as sigma (σ) bonding molecular orbital while the anti-bonding molecular orbital, is called σ^*
- "n" atomic orbitals combines to form "n" molecular orbitals.
- The filling of electron into the molecular orbitals takes place according to the

(i) Auf bau principle

(ii) Pauli's exclusion principle

(iii) Hund's rule

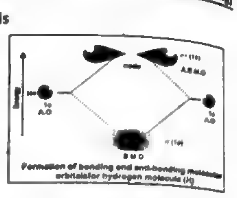
Difference between Bonding Molecular Orbital (BMO) and Anti-Bonding Molecular Orbital (ABMO)

Bonding Molecular Orbital (BMO)	Anti-Bonding Molecular Orbital (ABMO)
It is formed by the addition overlapping (constructive interference) of atomic orbitals	It is formed by the subtraction overlapping (destructive interference) of atomic orbitals
The wave function (ψ) of a BMO is given by $\psi_{BMO} = \psi_A + \psi_B$	The wave function (ψ) of an ABMO is given by $\psi_{ABMO} = \psi_A - \psi_B$
Its formation takes place when the lobes of atomic orbital have same sign.	Its formation takes place when the lobes of atomic orbital have different sign.
The energy of BMO is lesser than that of parent atomic orbitals.	The energy in A.B.M.O is higher than that of parent atomic orbitals.
The electron density is high in the region between the nuclei of the bonded atom.	The electron density is lower in the region between the nuclei of the bonded atom
Every electron in BMO contributes toward the attractive forces.	Every electron in A.B.M.O. contributes toward the repulsive forces
e.g. Sigma (σ) and Pi(π) in BMO.	e.g. Sigma (σ^*) and Pi(π^*) in A.B.M.O.

Formation of Bonding and Anti-Bonding Molecular Orbitals

(i) s and s-orbital overlap in H_2 molecule

The two electrons (one from each hydrogen atom), fill the low energy σ 1s orbital and have paired **spin** (↑↓), while the high energy σ^* 1s orbital remains empty. So far, we have considered s and s orbital overlaps for the formation of molecular orbitals of hydrogen molecule.



Formation of bonding and anti-bonding molecular orbitals for hydrogen molecule (H_2)

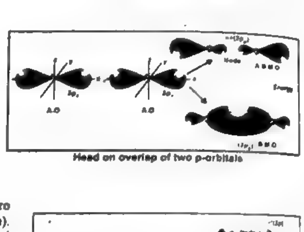
(ii) p and p orbital overlap

There are three 2p atomic orbitals directed along the three perpendicular x, y and z co-ordinates. For the formation of molecular orbitals from p-orbitals, two cases arise.

(a) Head on approach

Here, the two p-orbitals of the two atoms approaches along the same axis (i.e. p_x axis).

This combination of the atomic orbitals give rise to $\sigma(2p_x)$ bonding and $\sigma^*(2px)$ anti-bonding molecular orbitals. Both are symmetrical about the nuclear axis.



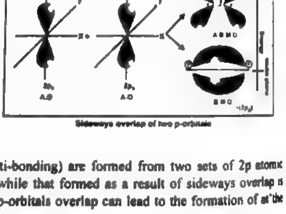
Head on overlap of two p-orbitals

(b) Sideways approach

When the axes of two p-orbitals (i.e. p_y and p_z orbitals) are parallel to each other, they interact to form molecular orbitals.

- The bonding molecular orbitals $\pi(2p_y)$ or $\pi(2p_z)$ have zero electron density on the nuclear axis (called the nodal plane). The electron density is uniformly distributed above and below the nodal plane.
- The anti-bonding molecular orbitals π^* (2py) and π^*(2pz) have the least electron density in the π Inter-nuclear region.

Since the $2p_y$ and $2p_z$ atomic orbitals are degenerate (having same energy), the π-molecular orbitals i.e. $\pi(2p_y)$ and $\pi(2p_z)$ are also degenerate. So, are also the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ molecular orbitals.

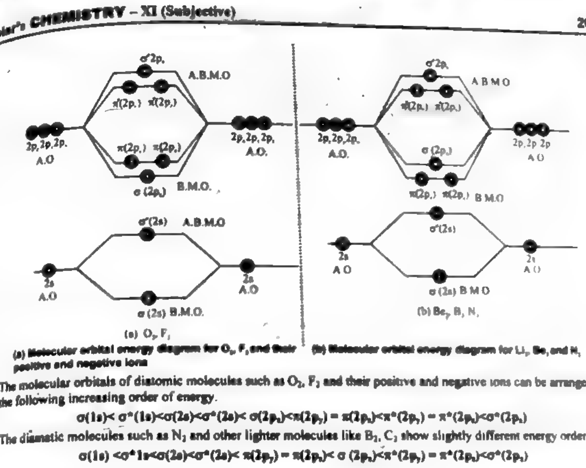


Sideways overlap of two p-orbitals

Overall six molecular orbitals (three bonding and three anti-bonding) are formed from two sets of 2p atomic orbitals. The bond formed as a result of linear overlap is σ bond, while that formed as a result of sideways overlap is called a π bond. As there are three bonding molecular orbitals, the p-orbitals overlap can lead to the formation of at the most three bonds one sigma and two π-bonds.

Relative energies of the molecular orbitals

The relative energies of the molecular orbitals formed from 2s and 2p atomic orbitals in the case of **homonuclear di-atomic molecules** as shown in figure. The energies of the molecular orbitals are determined by spectroscopic measurements.



(a) Molecular orbital energy diagram for O_2, F_2 and their positive and negative ions (b) Molecular orbital energy diagram for Li_2, Be_2 and N_2

- The molecular orbitals of diatomic molecules such as O_2, F_2 and their positive and negative ions can be arranged in the following increasing order of energy.

$$\sigma(1s)<\sigma^*(1s)<\sigma(2s)<\sigma^*(2s)<\sigma(2p_x)<\pi(2p_y)=\pi(2p_z)<\pi^*(2p_y)=\pi^*(2p_z)<\sigma^*(2p_x)$$

- The diatomic molecules such as N_2 and other lighter molecules like B_2, C_2 show slightly different energy order

$$\sigma(1s)<\sigma^*1s<\sigma(2s)<\sigma^*(2s)<\pi(2p_y)=\pi(2p_z)<\sigma(2p_x)<\pi^*(2p_y)=\pi^*(2p_z)<\sigma^*(2p_x)$$

Reason

It has been observed that in case of B_2, C_2 and N_2, $\sigma 2p_x$ is higher in energy than $\pi 2p_y = \pi 2p_z$ MOs. This reversal is due to mixing of 2s and $2p_x$ atomic orbitals.

Actually the energy difference of 2s and 2p atomic orbital is small. There is a possibility of mixing of these orbitals (i.e. hybridization of A.O.) as a result of which σ2s and σ^*2s MOs do not retain pure s-character. Similarly $\sigma 2p_x$ and $\sigma^* 2p_x$ MOs do not have pure p-character. All the four MOs acquire sp-character. Due to this mixing, their energies change in such a way that MOs σ2s and σ^*2s becomes more stable and are lowered in energy. MOs as $\sigma 2p_x$ and $\sigma^* 2p_x$ become less stable and are raised in energy. Since, πp-orbitals are not involved in mixing, so energy of $\pi 2p_y = \pi 2p_z$ remains unchanged. $\sigma 2p_x$ is raised to such an extent that it becomes higher in energy than π-bondings.

Anyhow, O_2 and F_2 do not do so. The reason is high energy difference of their 2s and 2p i.e. 1595 and 2078 $kJmol^{-1}$ for O_2 and F_2, respectively. These values are 554 $kJmol^{-1}$ for boron, 846 $kJmol^{-1}$ for carbon and 1195 $kJmol^{-1}$ for nitrogen. These energy differences have been calculated by spectroscopic techniques.

Bond order

"The number of bonds formed between two atoms after the atomic orbitals overlap, is called the bond order."

or

"Half of the difference between the number of bonding electrons and anti-bonding electrons is called the bond order."

$$\text{Bond order} = \frac{\text{Number of electrons in B.M.O} - \text{number of electrons in A.B.M.O}}{2}$$

Example: The number of bonds formed between H-atoms in Hydrogen molecule may be calculated as follows:

Number of electron in bonding molecular orbital = 2
Number of electron in anti-bonding molecular orbital = 0

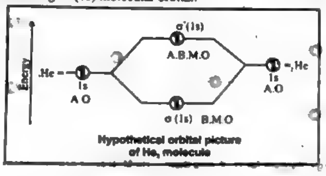
$$\text{Bond order} = \frac{2-0}{2} = 1$$

It is common practice that only MOs formed from valence orbitals are considered in bond order calculations.

Molecular Orbital structures of Some Diatomic Molecules:

(i) Helium, He_2

The electronic configuration of He is $1s^2$. The 1s orbitals of He-atoms combine to form one bonding $\sigma(1s)$ and one-anti-bonding σ^* (1s). Each He-atom contributes two electrons. Two electrons enter bonding molecular orbital $\sigma(1s)$ and the remaining two go to anti-bonding $\sigma^*(1s)$ molecular orbital.



Hypothetical orbital picture of He_2 molecule

Bond order

The bond order of He_2 is zero. i.e. $\frac{(2-2)}{2} = \frac{0}{2} = 0$ and thus He_2 molecule is not formed.

(ii) Nitrogen, N_2

Molecular orbital picture

The molecular orbital structure of N_2 molecules is shown

Energetics order of MOs

Electronic configuration of N_2 molecule is

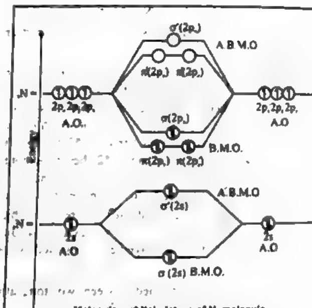
$$\sigma(1s^2) < \sigma^*(1s^2) < \sigma(2s^2) < \sigma^*(2s^2) < \pi(2p^2_y) = \pi(2p^2_z) < \sigma(2p^2_x) < \pi^*(2p_y) = \pi^*(2p_z) < \sigma^*(2p_x)$$

Bond order

From the electronic configuration of N_2, it is clear that six electrons enter into three outermost bonding orbitals while no electron enters into anti-bonding orbitals. Thus the bond order in N_2 molecule is $\frac{6-0}{2} = \frac{6}{2} = 3$, which corresponds to the triple bond consisting of one sigma and two π bonds.

Bond energy

The bond dissociation energy of N_2 is very high i.e. 941 $kJmol^{-1}$.



Molecular orbital picture of N_2 molecule

Diamagnetic property

Since no unpaired electron is present in MOs so N_2 molecule shows diamagnetic behaviour.

(iii) Oxygen, O_2

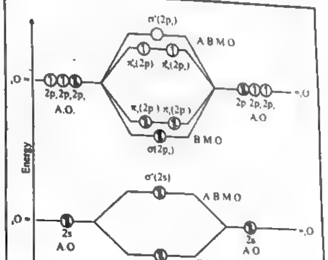
Molecular orbital picture

The molecular orbital structure of O_2 molecules is shown

Energetics order of MOs

Electronic configuration of O_2 molecule is

$$\sigma(1s^2) < \sigma^*(1s^2) < \sigma(2s^2) < \sigma^*(2s^2) < \sigma(2p_x^2) < \pi(2p_y^2) = \pi(2p_z^2) < \pi^*(2p_y^1) = \pi^*(2p_z^1) < \sigma^*2p_x.$$



Molecular orbital picture of O_2 molecule

Bond order

The bond order of O_2 is $\frac{6-2}{2} = 2$, which corresponds to a double bond.

Bond energy

This is consistent with large bond energy of 496 $kJmol^{-1}$ of oxygen molecule.

Cationic and anionic molecular ions of oxygen

When two more electrons are given to O_2, it becomes O_2^{2-}. The paramagnetism vanishes. Similarly in O_2^{2+}, the unpaired electrons are removed and paramagnetic property is no more there. Bond order O_2^{2-} and O_2^{2+} are also different from O_2 and are one and three, respectively.

Similarly M.O.T. justifies that F_2 has bond order of one and Ne does not make a bond with Ne.

Species	Bond Order
O_2	2
O_2^+	2½
O_2^-	1½
O_2^{2-}	1

Q. O_2 is a paramagnetic substance. Justify in the light of molecular orbital theory.

Ans. The filling of molecular orbitals leaves two unpaired electrons in each of the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ orbitals. Thus the electronic configuration of the molecular orbital accounts admirably for the paramagnetic properties of oxygen. This is one of the greatest successes of the molecular orbital theory. Liquid O_2 is attracted towards the magnet.

Table: Average Bond enthalpies of some important bonds (kJ/mol^{-1})

Bond	Bond energy ($kJmol^{-1}$)	Bond	Bond energy ($kJmol^{-1}$)	Bond	Bond energy ($kJmol^{-1}$)	Bond	Bond energy ($kJmol^{-1}$)
C—C	348	H—H	436	O—O	146	Si—H	323
C=C	614	H—F	567	O=O	495	Si—Si	226
C≡C	839	H—Cl	431	O—H	463	Si—C	301
C—H	413	H—Br	366	O—F	190	Si—O	368
C—N	293	H—I	299	O—Cl	203	F—H	155
C=N	615	N—N	163	O—I	234	Cl—F	253
C≡N	891	N=N	418	S—S	266	Cl—Cl	242
C—O	358	N≡N	941	S=S	418	Br—F	237
C=O	799	N—H	391	S=O	523	Br—Cl	218

$C=O$	1072	N—O	201	S—H	339	Br—Br	193
C—F	485	N—F	272	S—F	327	I—Cl	208
C—Cl	328	N—Cl	200	S—Cl	253	I—Br	175
C—Br	276	N—Br	243	S—Br	218	I—I	151
C—I	240						
C—S	259						

Q14. (a) Define bond energy. Explain various parameters which determine its strength.

Bond Energy (Bond Enthalpy)

"The average amount of energy required to break all bonds of a particular type in one mole of the substance is called the bond energy."

When a bond is formed between two atoms, energy is released. The same amount of energy is absorbed when the bond is broken to form neutral atoms. It is determined experimentally, by measuring the heat involved in a chemical reaction. It is also called bond enthalpy, as it is a measure of enthalpy change at 298K.

Enthalpy of atomization

"The enthalpy change in splitting a molecule into its component atoms is called enthalpy of atomization."

Units: The bond energy is given in $kJmol^{-1}$ which is the energy required to break an Avogadro's number (6.02×10^{23}) of bonds. It is also released when an Avogadro's number of bonds are formed.

Factors affecting bond energy

Bond energy is a measure of the strength of a bond. The strength of a bond depends upon the following factors.

(i) Electronegativity difference of bonded atoms

Greater the electronegativity difference of bonded atom, more will be the polarity of bond and higher will be its bond energy.

(ii) Sizes of the atoms

Bond energy decreases with increase in the atomic radii.

Bond	Bond Energy ($kJmol^{-1}$)
H – F	567
H – Cl	431
H – Br	366
H – I	299

(iii) Bond length

The bonds with higher bond energy values have shorter bond lengths. The bond energies of C to C bonds being in the order $C\equiv C > C=C > C-C$. Their bond lengths are in the reverse order i.e. $C-C > C=C > C\equiv C$.

(iv) Bond polarity

Generally, a polar covalent bond is stronger than a non-polar covalent bond.

Ionic Character and Bond Energy

Let us look at the bond energies of H-X type of compounds, where X=F, Cl, Br, I. In H–X, electrons are not equally shared between the bonded atoms. As halogen atom is more electronegative, the bonded pair is more attracted towards X atom and thereby polarity develops. This gives rise to additional attractive force for binding.

From the difference between experimental bond energies and those calculated by assuming equal sharing, it is possible to estimate relative electronegativities. The comparison of these values shows that the discrepancy is the greatest for HF and the least for HI.

Calculation of bond energy of HX molecule

Let us calculate, the increase in the strength of H-Cl bond, due to the ionic character present in it.

1. H_2 Molecule

(i) Bond energy of 1 mole of H_2

The H-H bond energy is 436 $kJmol^{-1}$

$H + H \rightarrow H_2 \quad \Delta H = -436kJmol^{-1}$

It means 436 kJ of heat is required to break the Avogadro's number of H_2 molecules into individual atoms

(ii) Bond energy per H_2 molecule

Thus, bond energy per bond is 72.42×10^{-23} kJ. This is obtained by dividing 436 by 6.02×10^{23}

(iii) Bond energy per H atom

As the bonding electron pair is equally shared between the two H-atoms. We can assume that each bonded H-atom contributes half of the bond energy i.e. 36.21×10^{-23} kJ.

2. Cl_2 Molecule

(i) Bond energy of 1 mole of Cl_2

The Cl–Cl bond energy is $240kJmol^{-1}$

$Cl + Cl \rightarrow Cl_2 \quad \Delta H = -240kJ\,mol^{-1}$

It means 240 kJ of heat is required to break the Avogadro's number of Cl_2 molecules into individual atoms

(ii) Bond energy per molecule of Cl_2

Thus, bond energy per bond is 39.86×10^{-23} kj. this is obtained by dividing 240 by 6.02×10^{23}

(iii) Bond energy per Cl atom

Therefore, each Cl-atom should contribute 19.93×10^{-23} kj to any bond, where sharing of an electron pair is equal

Table. Comparison of experimental and theoretical bond energies

Bond	Bond Energies ($kJ\,mol^{-1}$)			
	X = F	X = Cl	X = Br	X = I
X—X	155	242	193	151
H—X (Calculated)	293	336	311	291
H—X (Observed)	567	431	366	299
difference	274	95	55	8

3. Bond energy of HCl Molecule

Let us, now consider the bond in HCl. This bond is polar, but we consider the electron pair to be equally shared.

(i) Bond energy of 1 molecule of HCl

On adding up the bond energy contributions of H-atom and Cl-atom, we expect the bond energy of H-Cl to be 56.14×10^{-23} kJ per molecule which is the sum of 36.21×10^{-23} kJ and 19.93×10^{-23} kJ.

(ii) Bond energy of 1 mole of HCl

For Avogadro's number of HCl molecules, the calculated bond energy is $337.96kJ\,mole^{-1}$ which is obtained by multiplying 56.14×10^{-23} with 6.02×10^{23}.

- The experimentally found bond energy for HCl is 431 $kJ\,mol^{-1}$.

Conclusion

The observed bond energy is significantly greater than the calculated value and that means a more stable H-Cl bond. This stability is due to the ionic character present in the molecule. The decreasing polarity from HF to HI shows a trend toward equal sharing of electrons which is consistent with decreasing electronegativity from F to I.

Bond length

"The distance between the nuclei of two atoms forming a covalent bond is called the bond length."

Determination of bond length

The bond lengths are experimentally determined by physical techniques. The techniques may be electron diffraction, X-rays diffraction or spectral studies.

The covalent bond length between two atoms is often but not always independent of the nature of the molecules. For instance, in most of the aliphatic hydrocarbons, the C-C bond length is very close to 154 pm. The C-C bond length is also found to be the same in diamond.

Relationship between covalent radius and bond length

The covalent radii for different elements are almost additive in nature.

Examples

- The single bond radius of carbon is 77 pm which is half of the C-C bond length (154 pm).
- Similarly, the covalent radius of Cl is 99 pm i.e. one half of the Cl-Cl bond length (198 pm).
- So the bond length of C-Cl bond will be 77 + 99 = 176 pm.

Factors Affecting Bond Length

(i) Ionic character of a covalent bond

With an increase in electronegativity difference between the bonded atoms, the bond becomes shortened.

Example

Si-F bond length in SiF_4 is found to be 154-159 pm, whereas the addition of their covalent radii (Si = 117pm and F = 64 pm) give Si-F bond length to be equal to 181 pm. The calculated values are almost always higher due to electronegativity differences. The ionic character results in shortening of the bond length due to force of attraction between the polar ends.

(ii) Mode of hybridization

Moreover, hybridization scheme involved, also explains the shortening of bonds due to the predominant participation of s-orbitals. Since the 2s-orbital of carbon has smaller mean radius than the 2p-orbitals, it would be expected that greater the s character in the hybrid orbitals used, the shorter will be the bond distance.

Example

Thus, the C-C bond lengths are 154,133 and 120 pm for ethane, ethene and ethyne, respectively where s orbital contribution increases from sp^3 to sp. Further, π – bonding also reduces the internuclear bond distance.

(iii) Atomic radii

The bond length increase, as we move from top to bottom in a group of periodic table.

Examples

- In group IV-A of the periodic table, Si-Si bond length is more than C-C bond length.
- P-P bond length is much more than N-N bond length in group V-A.

As the atomic radii increase in a group (N to P or C to Si), the effect of the effective nuclear charge decreases on electrons. As a result the bond length will increase.

In the periodic table, shortening of bond lengths occurs from left to right in, a period. This can be attributed to the pull by nuclear charge with the same value of principal quantum number. Therefore, C-C bond length is greater than N-N bond length.

Table: Some selected bond lengths along with and hybridization of central atom

Compound	Hybridization	Bond	Bond length (pm)
BF_3 (Boron triflurode)	sp^2	B—F	130
BCl_3 (Boron trichloride)	sp^2	B—Cl	175
SiH_4 (Monosilane)	sp^3	Si—H	148
SiF_4 (Silicon tetrafluride)	sp^3	Si—F	155
C_2H_6 (Ethane)	sp^3	C—C	154
C_2H_4 (Ethene)	sp^2	C = C	133
C_2H_2 (Ethyne)	sp	C ≡ C	120
$(CH_3)_2C=O$ (Acetone)	sp^2	C = O	122

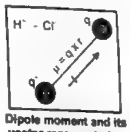
Q5. (a) Define dipole moment. Give its various units. Find relationship between Debye and mC. How does it help to find out the shapes of molecules.

Dipole Moment

"The product of electric charge (q) and the distance between the positive and negative centers (r) is called dipole moment."

$$\mu = \bar{q} \times \bar{r}$$

- It is a vector quantity because it has a magnitude as well as direction.
- The dipole moments of simple **heteronuclear diatomic molecules** like HCl, HBr, HI, CO, NO, etc. are directed from electropositive ends to electronegative ends.



Dipole moment and its vector representation

Symbol

Dipole Moment is shown with an arrow head having crossed tail.

Units

(i) The common unit of dipole moment is Debye (D).
(ii) In S.I. the units of dipole moment are mC.

Relationship between Debye (D) and mC

$$1D = 3.336 \times 10^{-30} mC$$

Explanation

Let us consider a hypothetical molecule ($A^+ - B^-$) or a unit negative charge separated from a unit-positive charge by distance r = 100 pm (1 Å), The dipole moment of such a molecule can be calculated by multiplying the distance 100 pm to charge of one electron or proton i.e. $1.6022 \times 10^{-19}C$.

$$\mu = (1.6022 \times 10^{-19}C) \times (100 \times 10^{-12}m)$$
$$= 1.6022 \times 10^{-29} mC.$$

Since $1D = 3.336 \times 10^{-30} mC$

$$\text{So } \mu = \frac{1.6022 \times 10^{-29} mC}{3.336 \times 10^{-30} mC}$$
$$\mu = 4.8D$$

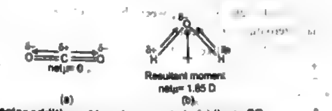
Dipole moments of some substances in Deybe

Compound	Dipole Moment (D)
H_2	0.00
HCl	1.03
HBr	0.78
HI	0.38
H_2O	1.85
H_2S	0.95
NH_3	1.49
SO_2	1.61
CO_2	0.00
CO	0.12
NO	0.16
H_2O_2	2.20
CH_4	0.00
CH_3F	1.81
CH_3Cl	1.45
CH_3Br	1.85
CH_3I	1.35
C_2H_5OH	1.69

Dipole moments for polyatomic molecules

If the molecule is poly atomic and contain two or more dipoles, then the net dipole moment is the resultant of the vector addition of the individual bond moments.

Examples



Vector addition of bond moments in (a) linear CO_2 molecule and (b) angular H_2O molecule

- A molecule having zero dipole moment is non polar
- Bond polarity ∝ dipole moment.

Applications of dipole moment

Dipole moment provides us two types of information about the molecule structure

1. Percentage Ionic character of a bond.
2. Angle between the bonds or the geometry of molecules.

1. Percentage Ionic character

From the experimentally determined dipole moments, the percentage ionic character in a bond can be calculated. For this purpose, we should know the actual dipole moment μ_{obs} of the molecule and actual bond length. The dipole of 100% ionic compound is represented as μ_{ionic}.

$$\%\text{age of ionic character} = \frac{\mu_{obs}}{\mu_{ionic}} \times 100$$

Example (1):

The observed dipole moment of HF is 1.90D. Find the percentage ionic character in H – F bond. The distance between the charges is 0.917×10^{-10} m. (Unit positive charge = 1.6022×10^{-19} C)

Ans. Given Data:

Observed dipole moment = μ_{obs} = 1.90D

Distance between charges = $r = 0.917 \times 10^{-10}$m

Unit positive charge = $q = 1.6022 \times 10^{-19}$C

Required:

Percentage ionic character in H – F bond = ?

Solution:

Let us suppose that HF molecule is 100% ionic. It means that H has full positive charge and F has full negative charge. To calculate ionic dipole moment, multiply the bond length with full charge of electron or proton i.e 1.6022×10^{-19}C. This dipole moment is called μ_{ionic}.

So, $\mu_{ionic} = q \times r$

$= (1.6022 \times 10^{-19}\text{C})(0.917 \times 10^{-10}\text{m})$

$= 1.469 \times 10^{-29}$ mC

Since

$1\text{D} = 3.336 \times 10^{-30}$mC

So, $\mu_{ionic} = \dfrac{1.469 \times 10^{-29}\ \text{mC}}{3.336 \times 10^{-30}\ \text{mC}}$

$= 4.4\text{D}$

The actual dipole moment is given as it is observed.

$\mu_{observed} = 1.90\text{D}$

Molecule	% ionic character
HF	43.2 %
HCl	17.7 %
HBr	12.1 %
HI	4.9 %

$$\text{Percentage ionic character} = \frac{\text{Observed dipole moment}}{\text{Ionic dipole moment}} \times 100$$

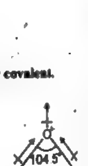
$$= \frac{1.90\text{D} \times 100}{4.4\text{D}}$$

$= 43.2\%$

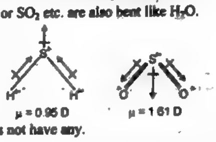
Hence, 43% of HF bond is ionic in nature and 57% covalent. The bond is predominantly covalent.

2. Bond angles or the geometry of molecules

(a) The dipole moment of water is 1.85D which ruled out its linear structure. The calculations show that water (H_2O) has an angular structure with a bond angle 104.5° between the two O—H bonds. A linear H_2O molecule (H—O—H) would have zero dipole moment.



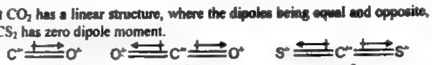
Similarly, triatomic molecules H_2S or SO_2 etc. are also bent like H_2O.



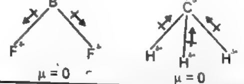
(b) CO has a dipole moment while CO_2 does not have any.

Reason

The reason is that CO_2 has a linear structure, where the dipoles being equal and opposite, cancel out each other's effect. Similarly CS_2 has zero dipole moment.



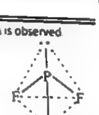
(c) Symmetrical triangular planer molecules of BF_3, $AlCl_3$ and perfectly tetrahedral molecules like CH_4, SiH_4, CCl_4 also have zero dipole moments. This is all due to the cancellation of individual bond moments.



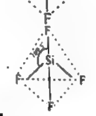
Q16. PF_3 is a polar molecule which has μ = 1.02 D and thus P-F bond is polar. Si is in the proximity of P in periodic table. It is expected that molecule is polar but SiF_4 has no dipole moment. Explain it.

Ans. If a molecule has μ = 0 then its structure is regular and symmetrical otherwise some value of μ is observed.

PF_3: It is a type of AB_4 with three bond pairs and one lone pair. Its structure will become trigonal pyramidal due to greater Lone pair - bond pair repulsions as compare to bond pair- bond pair repulsion. So a net effect of each polar bond is observed in the form of dipole moment = 1.02 D.



SiF_4: It is an AB_4 molecule with all four bond pairs showing equal repulsions. So regular tetrahedral shape is observed with μ = 0 and bond angle 109.5° although individual bond (Si-F) is polar.



THE EFFECT OF BONDING ON THE PROPERTIES OF COMPOUNDS

The properties of substances are characterized by the types of bonding present in them. Here, we shall consider the effects of the type of bond on physical and chemical properties of compounds.

1. Solubility

(a) Solubility of Ionic Compounds

Mostly, ionic compounds are soluble in water but insoluble in non-aqueous solvents. When a crystal of an ionic substance is placed in water, the polar water molecules detach the cations and anions from the crystal lattice by their electrostatic attraction. Thus, the ions are freed from the crystal lattice by hydration. This happens **when the hydration energy is greater than the lattice energy** and the ions are freed from their positions in the crystal. Many ionic compounds do not dissolve in water, as the attraction of water molecules cannot overcome the attraction between the ions. For the same reason, non-polar solvents like benzene and hexane do not dissolve ionic compounds.

(b) Solubility of Covalent Compounds

In general, covalent compounds dissolve easily in non-polar organic solvents (benzene, ether, etc.) Here, the attractive forces of solvent molecules are enough for overcoming the intermolecular forces of attraction. Mostly, covalent compounds are insoluble in water. However, some of them dissolve in water due to hydrogen bonding.

> **Q.** Covalent compounds show isomerism but ionic compounds do not. Justify

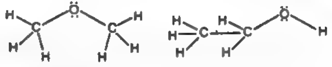
2. Isomerism

(a) Non- directional nature of ionic bonds

The ionic compounds involve electrostatic lines of forces between oppositely charged ions. Therefore, such bonds are **non-rigid and non-directional.** Because of this, ionic compounds do not exhibit the phenomenon of isomerism.

(b) Directional nature of covalent bonds

Covalent compounds are rigid and directional. This leads to the possibility of a variety of isomerism. For example, the compounds, C_2H_6O, shows structural isomerism.



Dimethyl ether Ethanol

3. Reaction Kinetics

(a) Speed of reactions of ionic compounds

The ionic compounds exist in the form of ions in an aqueous solution. The chemical reaction between ions occur rapidly. For example, addition of silver nitrate solution to sodium chloride solution produces a white precipitate of silver chloride instantaneously. The reaction is rapid because on mixing the solutions, no bonds have to be broken, only a new bond is formed. The ionic compounds have already been broken while forming their aqueous solutions.

(b) Speed of reaction of covalent compounds

Since, there is no strong electrical force to speed up a chemical reaction (like in ionic reaction), the covalent bonds are generally much slower to react as they involve bond breaking and making of bonds. The molecules undergo a chemical change as a whole. Covalent bonds react in a variety of ways and their reactivity depends upon the way a reaction proceed and the kind of a reaction.

KEY POINTS

1. Atoms combine together due to their inherent tendency to attain the nearest noble gas electronic configuration and the formation of a chemical bond always results in a decrease of energy.
2. The size of an atom is expressed in terms of atomic radius, ionic radius and covalent radius and van der Waals radius.
3. It is necessary to understand thermodynamic properties of elements. The minimum amount of energy required to remove an electron from an atom in gaseous state is called ionization energy. It depends upon the atomic size, nuclear charge and shielding effect of electrons. The electron affinity of an atom is the energy given out when an electron is added to a gaseous atom. The tendency of an atom to attract a shared pair of electrons to itself is called electronegativity. Fluorine, is the most electronegative atom and it has arbitrarily been given a value of 4.0.
4. The ionic bonds are formed by transfer of electron from one atom to another. Covalent bonds are formed by mutual sharing of electrons between combining atoms. After the formation of a coordinate covalent bond, there is no distinction between a covalent bond and a coordinate covalent bond.
5. A polar covalent bond is formed when atoms having different electronegativity values mutually share their electrons. Due to polarity, bonds become shorter and stronger and dipole moment may develop.
6. According to valence bond theory, the atomic orbitals overlap to form bonds but the individual character of the atomic orbitals are retained. The greater the overlap, the stronger will be the bond formed.
7. The VSEPR theory gives information about the general shapes and bond angles of molecules. It is bases upon repulsion between bonding and lone pairs of electrons, which tend to remain at maximum distance apart so that interaction between them is minimum. The concept provides an alternate way to explain various geometrical shapes of molecules.
8. The geometrical shapes and bond angles are better explained by different hybridization schemes, where different atomic orbitals are mixed to form hybrid orbitals.
9. According to molecular orbital theory, atomic orbitals overlap to form molecular orbitals. n atomic orbitals combine to form n molecular orbitals. Half of them are bonding molecular orbitals and half antibonding molecular orbitals. In this entirely new orbital that belongs to the whole molecule. The theory successfully explains bond order and paramagnetic property of O_2.
10. The bond energy in defined as the average amount of energy required to break all bonds of a particular type in one mole of the substance. It is a measure of the strength of the bond. Stronger the dipole of a bond, grater will be the bond energy.
11. The distance between the nuclei of two atoms forming a covalent bond is called bond length. In general, it is the sum of the covalent radii of the combined atoms.
12. The dipole moment may be defined as the product of electric charge (q) and the distance (r) between the two oppositely charged centres. It is a vector quantity as it has magnitude and direction. It plays a major role in

determining the % age ionic character of a covalent bond and the shapes of molecules. It has magnitude and direction.

13. Properties of substances are characterized by the type of bonds present in them.

SOLVED OBJECTIVE EXERCISE

Q. Select the correct statement:

(i) An ionic compound A^+B^- is most likely to be formed when:
(a) the ionization energy of A is high and electron affinity of B is low.
(b) the ionization energy of A is low and electron affinity of B is high.
(c) both ionization energy of A and electron affinity of B are high.
(d) both ionization energy of A and electron affinity of B are low.

(ii) The number of bonds in nitrogen molecule is:
(a) one σ and one π (b) one σ and two π
(c) three sigma only (d) two σ and one π

(iii) Which of the following statement is not correct regarding bonding molecular orbitals?
(a) Bonding molecular orbitals possess less energy than atomic orbital from which they are formed.
(b) Bonding molecular orbitals have low electron density between the two nuclei.
(c) Every electron in the bonding molecular orbitals contributes to the attraction between atoms.
(d) Bonding molecular orbitals are formed when electron waves undergo constructive interference.

(iv) Which of the following molecules has zero dipole moment?
(a) NH_3 (b) $CHCl_3$
(c) H_2O (d) BF_3

(v) Which of the hydrogen halides has the highest percentage of ionic character:
(a) HCl (b) HBr
(c) HF (d) HI

(vi) Which of the following species has unpaired electrons in anti-bonding molecular orbitals.
(a) O_2^{+2} (b) N_2^{-2}
(c) B_2 (d) F_2

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(b) The ionization energy of A is low and electron affinity of B is high.	A metal due to low ionization energy loses electron and form positive ion. On the other hand a non metal due to high electron affinity gains electron and forms negative ions. Ionic bond is formed between positive ion and negative ion.
(ii)	(b) one σ and two π	A triple bond is present in N_2 molecule in which one bond is sigma while two bonds are Pi.
(iii)	(b) Bonding molecular orbitals have low electron density between the two nuclei.	This is incorrect statement. Actually bonding molecular orbitals have high electron density between the two nuclei.
(iv)	(d) BF_3	BF_3 has a regular triangular planer structure so it has zero dipole moment

(v)	(c) HF	see table below
(vi)	(b) N_2^{-2}	In N_2^{-2} two unpaired electrons are present in anti bonding molecular orbitals.

Molecule	% Ionic character
HF	43.2 %
HCl	17.7 %
HBr	12.1 %
HI	4.9 %

Q2. Fill in the blanks:

(i) The tendency of atoms to attain maximum of ________ electrons in the valence shell is called completion of octet.

(ii) The geometrical shape of $SiCl_4$ and PCl_3 can be explained on the basis of ________ and ________ hybridizations.

(iii) The VSEPR theory stands for ________.

(iv) For N_2 molecule, the energy of $\sigma 2p_x$ orbital is ________ than $\pi 2p_y$ orbital.

(v) The paramagnetic property of O_2 is well explained on the basis of MOT in terms of the presence of ________ electrons in two anti-bonding molecular orbitals.

(vi) The values of dipole moment of CS_2 is ________ and for SO_2 is ________ D.

(vii) The bond order of N_2 is ________ while that of Ne_2 is ________.

ANSWERS

(i) eight	(ii) sp^3–sp^3
(iii) valence shell electron pair repulsion theory	(iv) higher
(v) unpaired	(vi) zero, 1.61 D
(vii) three, zero	

Q3. Tick true and false:

(i) The core of an atom is the atom minus its valence shell.

(ii) The molecules of nitrogen (N≡N) and acetylene HC≡CH are not Isoelectronic.

(iii) There are four coordinate covalent bonds in NH_4^+ ion.

(iv) A σ-bond is stronger than a π-bond and electrons of σ-bond are more diffused than π-bond.

(v) The bond energy of heteroatomic diatomic molecules increases with the decrease in electronegativities of the bonded atoms.

(vi) With increase in bond order, bond length decreases and bond strength increases.

(vii) The first ionization energy of the element rise steadily with the increasing atomic number from top to bottom in a group.

(viii) A double bond is stronger than a single bond and a triple bond is weaker than double bond.

(ix) The bonds formed between elements having the electronegativity difference more than 1.7 are said to be covalent in nature

(x) The repulsive force between the two bonding pairs is less than that between the two lone pairs.

(xi) The number of covalent bonds an atom can form is related to the number of unpaired electrons it has.

(xii) The rules which govern the filling of electrons into the atomic orbitals also govern the filling of electrons into molecular orbitals

ANSWERS

(i) True	(ii) False	(iii) False	(iv) False
(v) False	(vi) True	(vii) False	(viii) False
(ix) False	(x) True	(xi) True	(xii) True

SHORT ANSWERS TO EXERCISE

Q#. Explain the following with reasons:

(i) Bond distance is a compromise distance between two atoms.

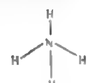
Ans. When two atoms come close to make a bond, the attractive and repulsive forces operate simultaneously. Attractive forces are responsible for decrease in potential energy of system, consequently increasing its stability While repulsive force increase the potential energy of system and stability decreases. Eventually a state comes when magnitude of attractive forces become maximum and potential energy minimum. So system gets maximum stability. At this distance a bond is formed between atoms so it is a **compromise distance**, **bond distance** or **bond length**.

At distance smaller than compromise distance, repulsive forces dominate and potential energy of system rapidly. For example, bond distance of H–H = 75.4 pm

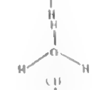
(ii) The distinction between a coordinate covalent bond and a covalent bond vanishes after bond formation in NH_4^+, H_3^+O and $CH_3NH_3^+$.

Ans. Structures of these molecules can be written as

In NH_4^+, covalent and coordinate covalent bonds are formed between N–H. Each bond has two electrons. Each bond length is equal, as all bonds are single bonds although their formation is different. Each bond has 75% covalent and 25% coordinate covalent character.



In H_3O^+, although one coordinate and two covalent bonds are observed between O–H yet their bond lengths are equal. Each bond is single bond between O–H and has 66% covalent and 33% coordinate character.



In $CH_3NH_3^+$: Two covalent bonds and one coordinate bond is present between N–H while one covalent bond is between CH_3–NH_3^+. All N–H bonds are similar with same bond length and 66% covalent while 33% coordinate character

Conclusion:

It is concluded that after formation, a coordinate covalent bond also behaves in the same manner as a covalent bond so distinction between them vanishes away.

(iii) The bond angles of H_2O and NH_3 are not 109.5° like that of CH_4 although O– and N– are sp^3 hybridized.

According to VSEPR theory, the shape of a molecule is decided on the basis of repulsions between of lone pairs and bond pairs around the central atom. Although N and O are sp^3 hybridized yet they differ in bonding from C compounds with sp^3 hybridization according to VSEPR theory.

The description of these molecules is as follows:

PROPERTIES	CH_4	NH_3	H_2O
Type of molecule	AB_4	AB_4	AB_4
No. of bond pairs	4	3	2
No. of lone pairs	0	1	2
Shape of molecule	Tetrahedral	Pyramidal	Angular
Bond angle	109.5°	107.5°	104
Reason of difference	Structure is regular due to only bond pair-bond pair	Structure is distorted due to lone pair as Lone pair-	Here due to two lone pairs, Lone pair-Lone pair

Properties	CH_4	NH_3	H_2O
	repulsions	Bond pair repulsion effects more than Bond pair-Bond pair repulsions so bond angle is reduced.	has a greater effect so angle is further reduced to 104°.

(v) The abnormality of bond length and bond strength is less in HI and prominent in HCl.

	HI molecule	HCl Molecule
Bond Energy (calc.)	291 kJ mol^{-1}	336 kJ mol^{-1}
Bond Energy (obs.)	299 kJ mol^{-1}	432 kJ mol^{-1}
Difference	8 kJ mol^{-1}	96 kJ mol^{-1}

The abnormality in bond strength, as shown by above data, is more prominent in HCl than in HI. Reason is that the more difference of electronegativity of H & Cl results in greater ionic character of HCl than expected.

As bond energy is inversely related to bond length, the calculated bond length of HCl is greater than observed bond length. Again the reason is, greater difference of electronegativity makes the bond of HCl stronger and shorter than that of HI.

(vi) Sodium chloride does not conduct electricity, but when electric current is passed through molten NaCl or its aqueous solution, electrolysis takes place.

Electrical conductance through different substance is due to

(a) mobile electrons (electronic or metallic conduction)

(b) free ions (electrolytic conduction)

In solid NaCl, oppositely charged ions are present at fixed positions due to strong electrostatic forces of attraction. Hence no free ion or mobile electron is available for electrical conductance. As a result solid NaCl is insulator.

On the other hand, in molten or aqueous solution state, Na^+ and Cl^- ions scattered and set free. As a result electrical conductance is possible (due to free ions).

(vii) The melting points, boiling points, heats of vaporization and heats of sublimation of electrovalent compounds are higher as compared with those of covalent compounds.

Ans. Electrovalent or ionic compounds have strong electrostatic forces of attraction between oppositely charged ions. On the other hand, covalent compounds generally exist in discrete molecule. Intermolecular forces in these molecules are much weaker than electrovalent compounds.

Thermodynamic parameters, like melting point, boiling point, heats of vaporization, heats of sublimation etc. are directly proportional to intermolecular forces present in compounds. Therefore ionic compounds have higher thermodynamic parameters than that of covalent compounds

For example:

Melting point of NaCl (ionic) = 801°C

Melting point of H_2O (covalent) = 0°C

NUMERICALS OF EXERCISE

Q14. (c) Calculate the bond energy of H-Br. The bond energy of H-H is 436 KJ mol^{-1} and that of Br-Br is 193 KJ mol^{-1}.

Ans. Give Data:

Bond energy of H-H = 436 kJ mol^{-1}

Bond energy of Br-Br = 193 kJ mol^{-1}

Requirement:

Bond energy of H-Br = ?

Solution: (i) 1st Method:

To calculate the bond energy of H-Br firstly calculate half the bond energies of H–H and Br–Br. Then they are added up.

Half of the bond energy of H–H $= \frac{436}{2}$

(i.e., Bond energy for one mole of H) = 218 kJ mol^{-1}

Half of the bond energy of Br-Br $= \frac{193}{2}$

(i.e., Bond energy for one mol of Br) = 96.5 kJ mol^{-1}

Bond energy of H–Br = Bond energy for H + bond energy for Br

= 218 + 96.5 = 314.5 kJ mol^{-1}

= **Bond energy of HBr = 314.5 kJ mol^{-1}**

(ii) 2nd Method:

Firstly Bond energy per molecule of H_2 and Br_2 is calculated by dividing with 6.02×10^{23} Then per atom Bond energy is calculated. After wards Bond energy of H and Br are added up, multiplied with 6.02×10^{23} to get Bond energy of HBr in kJ mol^{-1}.

Bond energy for one molecule of H_2 $= \frac{436}{6.02\times10^{23}}$

$= 7.24 \times 10^{-22}$ kJ

Bond energy for one molecule of Br_2 $= \frac{193}{6.02\times10^{23}}$

$= 3.20 \times 10^{-22}$

Bond energy per atom of H $= \frac{7.24\times10^{-22}}{2}$ kJ

$= 3.62 \times 10^{-22}$ kJ

Bond energy per atom of Br $= \frac{3.2\times10^{-22}}{2}$ kJ

$= 1.6 \times 10^{-22}$ kJ

Bond energy per molecule of HBr

= Bond energy of H atom + Bond energy. of Br-atom

$= 3.62 \times 10^{-22} + 1.6 \times 10^{-22}$

$= 5.22 \times 10^{-22}$ kJ

Bond energy. per mole of HBr

= Bond energy of one molecule HBr $\times 6.02 \times 10^{23}$

$= 5.22 \times 10^{-22} \times 6.02 \times 10^{23}$

= 314.42 kJ mol^{-1}

Bond energy for HBr = 314.42 kJ mol^{-1}

Q15. (b) The bond length of H-Br is 1.4×10^{-10} m. Its observed dipole moment is 0.79 D. Find the percentage ionic character of the bond. Unit positive charge = 1.6022×10^{-19} C and 1D = 3.336×10^{-30} mc.

Ans. Give data:

Bond length = 1.4×10^{-10} m

μ_{obs} = 0.79 D

q = 1.6022×10^{-19} C

Requirement:

μ_{ionic} = ?

% ionic character = ?

Solution:

$\mu_{ionic} = q \times r$

$= 1.6022 \times 10^{-19} \times 1.4 \times 10^{-10}$

$= 2.243 \times 10^{-29}$ Cm

1 Debye = 3.336×10^{-30} Cm

So $= \dfrac{2.243 \times 10^{-29}\,\text{Cm}}{3.336 \times 10^{-30}\,\text{Cm}}$

$= 6.72$ D

$\mu_{ionic} = 6.72$ D

$\mu_{obs} = 0.79$ D

% ionic character $= \dfrac{\mu_{obs}}{\mu_{ionic}} \times 100$

$= \dfrac{0.79}{6.72} \times 100$

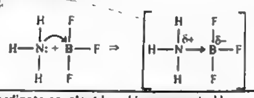
$= 11.75\%$

% Ionic character of HBr = 11.75%.

Additional Questions

Q. Differentiate between covalent and coordinate covalent bond.

Ans.

Covalent Bond	Coordinate Covalent Bond
(i) The bond which is formed by the mutual sharing of electrons between two atoms is called as covalent bond.	(i) A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms.
(ii) e.g. $H\bullet \times H \rightarrow H-H$; $\ddot{Cl}\cdot \times \ddot{Cl} \rightarrow Cl-Cl$	(ii) e.g. 
(iii) Single covalent bond is represented by a single line, double covalent bond by two lines and tripe covalent bond by tree lines.	(iii) Coordinate covalent bond is represented by an arrow pointing from the donor atom to the acceptor atom.

Comparison of sigma and pi bonds

	σ bond	π bond
1.	It is formed by the end to end overlap of two s-, one s- and one p-orbitals and two p-orbitals along their internuclear axis. It also results from end to end overlap of hybrid orbitals.	It is formed by side wise overlap of two p-orbitals.
2.	It determines the direction and extent of internuclear distance.	It has no primary effect on the direction of bond but shortens the internuclear distance
3.	It is a strong bond due to greater overlap of orbitals	It is a weak bond due to poor overlap of orbitals. It is formed when sigma bond already exists between atoms.
4.	The molecular sigma orbital consists of a single electron cloud symmetrically around the internuclear axis.	The molecular pi-orbital consists of two electron clouds , one above and one below the plane of the bonded atoms.
5.	There can be free rotation of atoms around the s - bond.	As the electron cloud overlap is above and below the plane of atoms, free rotation is not possible around pi-bond.

Important Previous Board Questions

Q. Why a polar covalent bond is stronger than a non-polar covalent bond?

Q. Why do noble gases not exist in diatomic form?

Q. Why the second ionization energy value is always higher than first ionization energy value?

Q. Why electron affinity value of II-A group are less than those of 1-A?

Q. CO_2 is a non-polar molecule although its bonds are polar. Why?

Q. Why nitrogen molecule is diamagnetic?

Q. Why the ionization energies of III-A group elements are less as compared to II-A although the values should increase form left to the right in a period?

Q. Why the first electron affinity for most of the elements is negative. While the second electron affinity for all the elements are positive?

Q. Why the dipole moment of CH_4 is zero?

Q. Why the covalent bonds are directional?

Q. What is Octet Rule? Why certain elements do not obey it? What is the relationship between the bond energy, bond strength and bond length?

Q. Phosphonium ion has different types of bonds. Justify it.

For Answers study Scholar's CHEMISTRY (Objective) XI

Chapter 7

THERMO CHEMISTRY

Thermo Chemistry

"The branch of chemistry in which we study heat changes accompanying a chemical reaction is called thermo-chemistry."

Substances exist, because they possess energy. Different substances have different energies associated with them. Due to this reason, total energy of reactants is never equal to that of products. In a chemical reaction, the energy in the form of heat will either be absorbed or evolved.

Heat of reaction

"The amount of heat which is absorbed or evolved during a chemical reaction is called heat of reaction."

Enthalpy of reaction

"The amount of heat which is evolved or absorbed during a chemical reaction at constant temperature and pressure is called enthalpy of reaction."

ΔH = -ive (for exothermic reaction)

ΔH = +ive (for endothermic reaction)

Examples

(i) The formation of water from hydrogen and oxygen is an exothermic process.

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H = -285.58\ kJ\ mol^{-1}$

(ii) The combustion of carbon in oxygen:

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.7\ kJ\ mol^{-1}$

(iii) In the Haber's process, the formation of ammonia is also an exothermic reaction.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -41.6 kJ\ mol^{-1}$

(iv) The decomposition of water into oxygen and hydrogen is an endothermic reaction.

$H_2O_{(l)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)} \quad \Delta H = +285.58 kJ\ mol^{-1}$

(v) When one mole of nitrogen combines with one mole of oxygen to yield nitrogen oxide (NO), 180.51 kJ of heat is absorbed by the system and the reaction is endothermic.

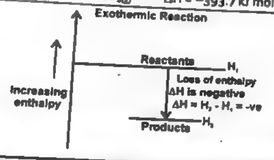
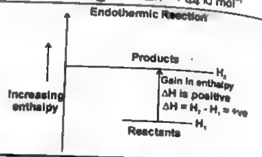
$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)} \quad \Delta H = +180.51 kJ\ mol^{-1}$

The subject matter of thermochemistry is based on the first law of thermodynamics.

The subject has an important practical utility as it gives us information about the energy or heat contents of compounds, a knowledge of which is necessary for the study of chemical bonding and chemical equilibrium. The scope of thermochemistry is limited mainly, because only a few of many chemical reactions are such, whose heats of reaction can be accurately measured.

Differentiate between Exothermic and Endothermic Reactions

Exothermic Reactions	Endothermic Reactions
(i) The reactions in which heat is evolved from the system.	(i) The reactions in which heat is absorbed by the system
(ii) Heat content of products is less than that of reactants. $H_R > H_P$	(ii) Heat content of reactants is less than that of products $H_P > H_R$
(iii) ΔH = -ive	(iii) ΔH = + ive
(iv) The number of bonds formed is greater than bonds	(iv) The number of bonds breakage is greater than bonds

breakage during the reaction.	formed during the reaction.
(v) The temperature of the system rises and eventually heat flows from the system to the surroundings.	(v) The temperature of the system falls and eventually heat flows from the surroundings to the system.
(vi) Most spontaneous reactions are exothermic.	(vi) Most non-spontaneous reactions are endothermic.
Examples $H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H = -285.5\ kJ\ mol^{-1}$ $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7\ kJ\ mol^{-1}$	**Examples** $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H = +180.51\ kJ\ mol^{-1}$ $H_2O_{(l)} \longrightarrow H_2O_{(g)}$ $\Delta H = +44\ kJ\ mol^{-1}$
	

Q6. (a) What are spontaneous and non-spontaneous reactions? Give examples.

Spontaneous Reaction or Process

"A process which takes place on its own without any outside assistance and moves from a non-equilibrium state to equilibrium state is called spontaneous reaction or natural process."

A spontaneous reaction is unidirectional, irreversible and real. Spontaneous reactions are mostly exothermic.

Examples

(i) Water flows from higher level to the lower level. The flow cannot be reversed without some external aid.

(ii) Neutralization of a strong acid with a strong base is a spontaneous acid base reaction.

$$NaOH_{(aq)} + HCl_{(aq)} \rightleftharpoons NaCl_{(aq)} + H_2O_{(\ell)}$$

(iii) When a piece of zinc is added to the copper sulphate solution, blue-colour of the solution disappears due to the spontaneous redox reaction.

$$CuSO_{4(aq)} + Zn_{(s)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

(iv) Transfer of heat from hotter to colder body.

A reaction will also be called a spontaneous process, if it needs energy to start with, but once it is started, then it proceeds on its own. Burning of coal and hydrocarbon in air are examples of such spontaneous reactions. A piece of coal does not burn in air on its own rather the reaction is initiated by a spark and once coal starts burning, then the reaction goes spontaneously to completion.

Non-Spontaneous Reaction or Process

"A process which does not take place on its own and need external assistance to carry out is called non-spontaneous process."

A non-spontaneous reaction is:

- Reversible processes constitute a limiting case between spontaneous and non-spontaneous processes.
- Some non-spontaneous processes can be made to take place by supplying energy to the system from external source.

Examples

(i) Pumping of water uphill.

(ii) Transfer of heat from cold interior part of the refrigerator to the hot surroundings.

(iii) When nitrogen reacts with oxygen, nitric oxide is formed. This reaction takes place by the absorbance of heat. Although, N_2 and O_2 are present in air, but they do not react chemically at ordinary conditions. The reaction takes place when the energy is provided by lightning.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \quad \text{(Non – spontaneous reaction)}$$

Some exceptional cases

Our common experience shows that the spontaneous reactions proceed with a decrease in the energy. We might expect, therefore, that a chemical reaction would proceed spontaneously if the reaction system decreases its energy by transferring heat to its surroundings. In other words, we might expect that all the exothermic reactions are spontaneous. This is usually true but not always. There are many endothermic changes that proceed spontaneously although they absorb heat.

Examples

(i) Evaporation of water.

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H = +44.0\ kJ\ mol^{-1}$$

(ii) Ammonium chloride dissolves in water and this process is also endothermic.

$$NH_4Cl_{(s)} \rightleftharpoons NH^{+}_{4(aq)} + Cl^{-}_{(aq)} \qquad \Delta H = +15.1\ kJ\ mol^{-1}$$

Determination of spontaneity of a reaction

The energy change alone cannot help us to predict, whether a reaction will occur spontaneously or not. To predict whether a reaction will occur spontaneously or not, it is necessary to study the free energy change (ΔG) of the system. The concept of free energy can help us to understand the processes in terms of entropy chain.

ΔG = +ve (for non-spontaneous)

ΔG = –ve (for spontaneous)

Q6. (b) Explain that burning of a candle is a spontaneous process.

Ans. A reaction which takes place on its own without outside assistance and moves from non-equilibrium state to equilibrium state is called spontaneous reaction.

The candle is made up of wax which is a hydrocarbon. On combustion it converts into carbon dioxide and steam.

$$\text{Wax + Oxygen} \longrightarrow \text{Carbon dioxide + Steam} \qquad \Delta H = -ve$$

Although burning of candle needs an initiation but once combustion is started then it proceeds on its own in the presence of wax and oxygen.

So we can say that burning of candle is a spontaneous process.

Q6c. Is it true that a non-spontaneous process never happens in the universe? Explain it.

Ans. No, it is not true. Sometimes a non-spontaneous reaction can happen in universe.

Sometime conditions are not suitable for a particular reaction but at some other time same reaction can happen due to suitable natural conditions. For example, nitrogen and oxygen are present in air and are unreactive under normal atmospheric conditions but during thunderstorm and lightening, electric spark enables these gases to react with each other as their reaction is highly endothermic.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \quad \Delta H = +180\ kJ\ mol^{-1}$$

So it is an example of a natural non-spontaneous reaction.

Q4. Define the following terms and give examples.

(i)	System	(ii)	Surrounding	(iii)	Boundary
(iv)	State function	(v)	Internal energy		

System

"Anything (materials) under test in the laboratory or under consideration in the classroom for the purpose of argument is called a system." or

"Any portion of the universe which is under study is called a system."

Examples

(i) In a reaction between Zn and $CuSO_4$, the contents of container are systems.

(ii) A cup of water is a system.

(iii) A book under discussion is a system.

Surroundings

"Around the system, all the remaining parts of the universe are called its surroundings."

Examples

(i) In the reaction between Zn and $CuSO_4$ solution, the flask, the air are the surroundings.

(ii) A cup of water is a system where as table on which it is lying, air etc. are the surroundings

System and Surroundings

Boundary

"The real or imaginary surface separating the system from the surroundings is called boundary."

Example

In the reaction between Zn and $CuSO_4$, the flask and air are surroundings and the surface of flask is boundary.

State

"The description of a system before and after a change is called state of system."

or

"The conditions of a system are called state of system."

Explanation

Let us consider a beaker containing water. It will be a system having certain temperature and volume. This initial condition of the system may be called the initial state. Suppose we heat the beakers. The system will undergo a change after heating. The final condition of the system may now be called the final state of system. By comparing both initial and final states of the system, we can describe the change taking place in system.

Let T_1 and T_2 denote the temperature before and after heating respectively. The change in temperature, ΔT may be represented as

$$\Delta T = \text{Final temperature} - \text{Initial temperature}$$

$$\Delta T = T_2 - T_1$$

State Function

"A macroscopic property of a system which has some definite values for initial and final states, and which is independent of the path adopted to bring about a change is called state function."

By convention, we use capital letters as symbols for a state function.

Examples are pressure (P), temperature (T), volume (V), internal Energy (E), enthalpy (H) etc.

Important point

Work done and heat are not state functions because they depend upon the path followed to bring about the change.

Explanation

Let us suppose V_1 is the initial volume of the gas. A change is brought about in the gas and its final volume becomes V_2. The change in volume (ΔV) of the gas is given by:

$$\Delta V = V_2 - V_1$$

Now, this change in volume of the gas can be brought about either by changing temperature or pressure of the gas. Since V is a state function, so ΔV will be independent of the way the volume of the gas has been changed. It will only depend upon the initial and final volumes of the gas.

Internal Energy (E)

"The total of all the possible kinds of energies of the system is called internal energy."

$$E = K.E + P.E$$

- The absolute values of internal energy can not be determined but change in internal energy (ΔE) can be measured.
- ΔE is a state function.

Explanation

A system containing some quantity of matter has definite amount of energy present in it. This energy is the sum of kinetic as well as potential energies of the particles contained in the system. The kinetic energy is due to the translational, rotational and vibrational movements of particles.

(a) Translational motion of He gas molecules | (b) A diatomic molecule of H_2 is vibrating | (c) A tetraatomic molecule say BF_3 is rotating on an axis

The potential energy accounts for all types of attractive forces present in the system. These attractive forces include all types of bonds and van der Waals's forces present between the particles. The total of all the possible kinds of energies of the system is called internal energy.

Note: Diatomic molecules have translational motions as well. Anyhow triatomic and higher molecules have translational, vibrational and rotational motions.

Fundamental ways of transferring energy

There are two fundamental ways of transferring energy to or from a system.

(i) Heat

(ii) Work

Heat

"The quantity of energy that flows across the boundary of a system during a change in its state due to the difference in temperature between the system and the surroundings is called heat (q)."

- It is not a property of a system.
- It is not a state function.

Sign convension

- q = +ve (when system absorbs heat from the surroundings)
- q = –ve (when system releases heat to the surroundings)

Work

"The product of force and displacement is called work (w)."

$$W = F \times S$$

- It is not a state function.
- In SI, the unit of work is 'Joules'.

Sign convension

w = –ve (when work is done by the system)

w = +ve (when work is done on the system)

Standard conditions are:

- a pressure of 1 atm
- a temperature 298K (25°C) is usually used
- a concentration of 1 mol dm^{-3} (for aqueous solutions).
- a standard state is the physical state of a substance under standard conditions.

Explanation

There are different kinds of work. The type of work we most commonly encounter in chemistry is pressure-volume work. For example, expansion can occur when a gas is evolved during a chemical reaction.

Pressure - volume work during expansion of a gas.

In such cases, the work done by the system is given by

$$w = -P\Delta V$$

(In pressure volume work force becomes pressure and distance becomes volume change.)
Where 'P' is the external pressure and 'ΔV' is the change in volume.

Q7. (a) What is first law of thermo dynamics? How does it explain?

(i) $q_v = \Delta E$ (ii) $q_p = \Delta H$

Ans.

First Law of Thermodynamics

"Energy can neither be created nor destroyed during a chemical reaction but can be changed from one form to another."

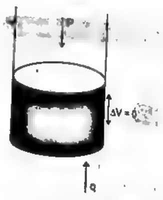
or

"The total energy of a system and its surroundings remain constant."

It is also called law of conservation of energy.

Mathematical form

$$\Delta E = q + w$$



Explanation

Consider a gas enclosed in a cylinder having a frictionless piston. When a quantity of heat 'q' is supplied to the system, its internal energy 'E_1' changes to 'E_2' and piston moves upwards. The change in the internal energy ΔE is given by the following equation:

$$\Delta E = E_2 - E_1 = q + w$$
$$\Delta E = q + w$$

In this equation, 'q' represents the amount of heat absorbed by the system and 'w' is the work done on the system in moving the piston up.

If 'w' is the pressure-volume work, then the above expression assumes the following form:

$$\Delta E = q + P\Delta V \qquad \therefore w = P\Delta V$$

When the piston is kept in its original position or the volume is not allowed to change, then

$$\Delta V = 0$$

and then

$$\Delta E = q_v$$

Conclusion

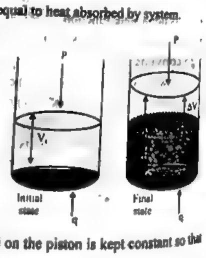
This shows that a change in the internal energy of a system, at constant volume is equal to heat absorbed by system.

Enthalpy (H)

"The sum of internal energy (E) and the product of pressure and volume (PV) is called enthalpy of the system."

Formula

$$H = E + PV$$



Initial state

Final state

Important points

- Enthalpy is a state function.
- Enthalpy is measured in "Joules."
- It is not possible to measure the enthalpy of the system in a given state. However, change in enthalpy (ΔH) can be measured for a change in the state of system.

Prove that $\Delta H = q_p$

Consider a gas enclosed in a cylinder having a piston. The external pressure on the piston is kept constant so that $\Delta P = 0$.

Now when heat 'q' is given to the system, a part of this heat is used to increase its internal energy and the rest is used to do work on the surroundings by increasing volume from V_1 to V_2.

According to definition of enthalpy

$$H = E + PV$$

A change in enthalpy of a system is written as

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + \Delta PV + P\Delta V$$

Since, the gas is kept at constant pressure *i.e.*, $\Delta P = 0$

Hence $\Delta H = \Delta E + P\Delta V$

For Liquids and Solids

In case of liquids and solids, the changes in state do not cause significant volume change i.e. $\Delta V = 0$. For such process, ΔE and ΔH are approximately the same *i.e.* $\Delta H \approx \Delta E$

According to first law of thermodynamics:

$$\Delta E = q + w$$

If w is pressure – volume work done by system, then

$$w = -P\Delta V$$
$$\Delta E = q - P\Delta V$$

Putting the value of ΔE in equation:

$$\Delta H = q - P\Delta V + P\Delta V$$
$$\Delta H = q$$

Since pressure is kept constant then

$$\Delta H = q_p$$

Conclusion

This shows that change in enthalpy is equal to heat of reaction at constant pressure. The reactions are carried out at constant pressure more frequently than at constant volume. So working with ΔH is rather more convenient than ΔE

Q6. Is it true that ΔH is equal to ΔE for reaction taking place in solution form?

Ans. According to equation for enthalpy change.

$$\Delta H = \Delta E + P\Delta V$$

Where

ΔH is enthalpy change,
ΔE is internal energy change, P is pressure and
ΔV is change in volume of system.

For liquids and solution, the volume change is negligible by applying heat

So $\Delta V = 0$

Hence $P\Delta V = 0$

And. $\Delta H = \Delta E$

So this equation show that it is true that $\Delta H = \Delta E$ for reaction taking place in solution form

Q5. (a) Define the following enthalpies and give two examples of each.

(i)	**Standard enthalpy of reaction**	**(ii)**	**Standard enthalpy of combustion**
(iii)	**Standard enthalpy of atomization**	**(iv)**	**Standard enthalpy of solution**
(v)	**Standard enthalpy of formation**	**(vi)**	**Standard enthalpy of neutralization**

Enthalpy of a Reaction

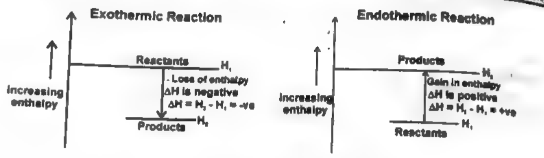
"The enthalpy change which occurs when the certain number of moles of reactants react together completely to give the products under standard conditions i.e. 25°C and one atmosphere pressure is called standard enthalpy of reaction ($\Delta H°$)."

Units

Its units are kJ mole^{-1}.

For an element, the standard enthalpy change of formation is defined as zero.

The formation of $H_{2(g)}$ from $H_{2(g)}$ does not involve a chemical change so there is no enthalpy change



Enthalpy changes in thermochemical reactions

Example

$$H_{2(g)} + 1/2\ O_{2(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H^\circ = -285.8\ kJ\ mol^{-1}$$

$-285.8 kJ\ mol^{-1}$ is standard enthalpy of reaction.

Enthalpy of Formation

"The amount of heat evolved or absorbed when one mole of compound is formed from its elements under standard conditions of temperature and pressure is called standard enthalpy of formation (ΔH_f°) of a compound."

- State symbols give the physical states of each species in a reaction: gaseous state, (g); liquid state (ℓ); solid state, (s); aqueous solution, (aq)

Important points

- All the substances involved are in their standard physical states.
- The reaction is carried at standard conditions i.e. at 25°C (298K) and one atmospheric pressure.
- Its units are $kJ\ mol^{-1}$.

Examples: (i) The enthalpy of formation, (ΔH_f°) for $MgO_{(s)}$ is $-692 kJ\ mol^{-1}$

$$Mg_{(s)} + \tfrac{1}{2}O_{2(g)} \longrightarrow MgO_{(s)} \quad \Delta H_f^\circ = -692\ kJ\ mol^{-1}$$

(ii) When carbon reacts with oxygen to form CO_2, 393.7 $kJ\ mol^{-1}$ of energy is released. It is ΔH_f° of $CO_{2(g)}$.

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_f^\circ = -393.7\ kJ\ mol^{-1}$$

Enthalpy of Atomization

"The amount of heat absorbed when one mole of gaseous atoms are formed from the element under standard conditions is called standard enthalpy of atomization of that element(ΔH°_{at})."

- Its units are $kJ\ mol^{-1}$.

Example: The standard enthalpy of atomization of hydrogen is

$$\tfrac{1}{2}H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H^\circ_{at} = 218\ kJ\ mol^{-1}$$

A wide range of experimental techniques are available for determining enthalpies of atomization of elements.

Enthalpy of Neutralization

"The amount of heat evolved when one mole of hydrogen ions (H^+) from an acid, react with one mole of hydroxide ions (OH^-) from a base to form one mole of water under standard conditions is called standard enthalpy of neutralization (ΔH_n°)."

For weak acids, this enthalpy change is less exothermic because some input of energy is required to dissociate the acid because a weak acid only partially dissociates into ions.

- Its units are $kJ\ mol^{-1}$

Example

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$
$$NaOH_{(aq)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$

When these solutions are mixed together during the process of neutralization, the only change that actually occurs is the formation of water molecules leaving the sodium ions and the chloride ions as free ions in solution. Thus, enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components

$$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} \qquad \Delta H_n^\circ = -57.4\ kJ\ mol^{-1}$$

Enthalpy of neutralization for any strong acid with a strong base is approximately the same i.e. -57.4 $kJ\ mole^{-1}$

Enthalpy of Combustion

"The amount of heat evolved when one mole of a substance is completely burnt in excess of oxygen under standard conditions is called standard enthalpy of combustion of a substance (ΔH_c°)."

- Its units are $kJ\ mol^{-1}$.

Example

Standard enthalpy of ethanol is $-1368\ kJ\ mol^{-1}$

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \quad \Delta H_c^\circ = -1368\ kJ\ mol^{-1}$$

Enthalpy of Solution

"The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change is called standard enthalpy of solution (ΔH°_{sol})."

- It units are $kJ\ mol^{-1}$.

Examples

(i) Enthalpy of a solution of NH_4Cl = +16.2 $kJ\ mol^{-1}$.

(ii) Enthalpy of solution of Na_2CO_3 = −25.0 $kJ\ mol^{-1}$.

Measurement of Enthalpy of a Reaction

Exothermic and endothermic reactions can easily be detected by observing the temperature of the reaction vessel before and after the reaction, as long as the heat of reaction evolved or absorbed is considerable. More accurate values of ΔH can be detected by using:

1. Glass calorimeter
2. Bomb calorimeter

1. Glass Calorimeter

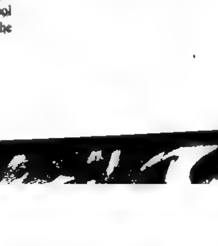
Objective

An ordinary glass calorimeter can be used to determine the value of ΔH.

Instrumentation

This usual type of calorimeter is basically an insulated container. It consists of:

- Stirrer
- Thermometer
- Lid
- Wool or cotton is present between the two beakers.



Glass calorimeter to measure enthalpy change of reactions

Working

Reactants in stoichiometric amounts are placed in calorimeter. When the reaction proceeds, the heat energy evolved or absorbed will either warm or cool the system. The temperature of the system is recorded before (T_1) and after the chemical reaction (T_2). Now calculate the temperature change (ΔT).

$$\Delta T = T_2 - T_1$$

Calculations

Knowing the change in temperature, the mass of reactants present and the specific heat of water, we can calculate the quantity of heat 'q' evolved or absorbed during the reaction. Thus

$$q = m \times s \times \Delta T$$

where m = mass of reactants
s = specific heat of reaction mixture
ΔT = change in temperature

Heat capacity

"The product of mass and specific heat of water is called heat capacity of the whole system."

$$c = m \times s$$

Bomb Calorimeter

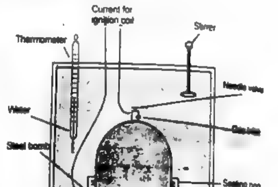
Objective

A bomb calorimeter is usually used for the accurate determination of the enthalpy of combustion for food, fuel and other compounds.

Instrumentation

A bomb calorimeter consists of a strong cylindrical steel vessel usually lined with enamel to prevent corrosion. A known mass (about 1 g) is usually placed in a platinum crucible inside the bomb. The lid is screwed tightly and oxygen is provided in it through a valve until the pressure inside is about 20 atm.

After closing the screw valve, the bomb calorimeter is then immersed in a known mass of water in a well-insulated calorimeter. Then it is allowed to attain a steady temperature.



Bomb calorimeter

Working

The initial temperature is measured by using the thermometer present in the calorimeter. The test substance is then, ignited, electrically by passing the current through the ignition coil. The temperature of water, which is stirred continuously, is recorded at 30 sec intervals.

The specific heat capacity of a substance is the energy required to raise the temperature of 1 g of a substance by 1°C.

Calculation

From the increase of temperature (ΔT) heat capacity (c) in kJK^{-1} of bomb calorimeter including bomb, water etc., we can calculate the enthalpy of combustion.

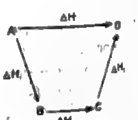
$$q = c \times \Delta T$$

The heat capacity (c) of a body or system is defined as the quantity of heat required to change its temperature by 1 K.

HESS'S LAW OF CONSTANT HEAT SUMMATION

Statement

"If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same."



Explanation

Let A can be converted to D directly in a single step and heat evolved is ΔH. If the reaction can have a route from $A \rightarrow B \rightarrow C$ as shown below.

According to Hess's law, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Mathematically, $\Sigma\Delta H(\text{cycle}) = 0$

Of course, Hess's law is simply an application of the more fundamental law of conservation of energy. So $\Sigma\Delta H$ (cycle) = 0. It means that if one goes from A to D directly and comes back to A through B and C then $\Delta H = 0$.

Examples

(i) Formation of Na_2CO_3

Single step process

$$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \quad \Delta H = -89.08\ kJ$$

Two steps process

$$NaOH_{(aq)} + CO_{2(g)} \longrightarrow NaHCO_{3(aq)} \quad \Delta H_1 = -48.06\ kJ$$

$$NaHCO_{3(aq)} + NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \quad \Delta H_2 = -41.02\ kJ$$

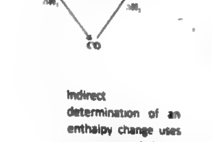
According to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2$$

Putting the values of ΔH, ΔH_1 and ΔH_2 in the equation.

$-89.08 = -48.06 - 41.02$
$-89.08 = -89.08\ kJ$

(ii) Enthalpy of Formation of CO



Single step process

$$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_{(graphite)} = -393.7\ kJ\ mol^{-1}$$

Two steps process

$$C_{(graphite)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H\ (CO) = \quad ?$$

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_2(CO_2) = -283\ kJ\ mol^{-1}$$

According to Hess's law

$\Delta H = \Delta H_1 + \Delta H_2$
$\Delta H_1 = \Delta H_2 - \Delta H$
$= -393 - (-283)$
$= -110\ kJ\ mol^{-1}$

So, the enthalpy change for the formation of $CO_{(g)} = -110.0\ kJ\ mol^{-1}$

Indirect determination of an enthalpy change uses an energy cycle based on Hess' Law.
This method is used when the reaction is very difficult to carry and related reactions can be measured more easily.

Applications of Hess's law

It is used in indirect measurement of:

1. Heat of combustion
2. Heat of formation
3. Heat of neutralization
4. Lattice energy of ionic compound

Explanation

There are many compounds, which ΔH cannot be measured directly by calorimetric method. The reason is, that some compounds like tetrachloromethane (CCl_4), cannot be prepared directly by combining carbon and chlorine. Similarly, it does not decompose easily into its constituent elements. In the same way, boron oxide (B_2O_3) and aluminum oxide (Al_2O_3) provide problems for the measurement of standard enthalpies of their formation. In these cases, it is difficult to burn these elements completely in oxygen, because a protective layer of oxides covers the surface of the unreacted element. Similarly, heat of formation of CO cannot be measured directly due to the formation of CO_2 with it.

Q.h. Hess's law helps us to calculate the heats of those reactions which cannot be normally carried out in the laboratory. Explain it.

Ans. Heat of reactions can be measured:

(i) Practically by means of calorimeter
(ii) Theoretically by means of Hess's law of constant heat summation.

By using Hess's law, we can calculate the heats of those reactions which are:

(i) Completed in more than one steps.
(ii) Too fast (vigorous).
(iii) Too slow to complete

In indirect measurement of enthalpy for a reaction which is not determined practically e.g.,

(a) enthalpy of formation of Al_2O_3
(b) enthalpy of combustion of CO
(c) Lattice enthalpy of ionic substances.

Q12(a) What is lattice energy?

Ans. "Enthalpy of formation of one mole of crystalline ionic compound from gaseous ions under standard conditions is called lattice energy."

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} \qquad \Delta H_{lat} = -787\ kJ\ mol^{-1}$$

or

"Energy required to break one mole of crystalline ionic compound into its gaseous ions at standard conditions is called lattice energy."

$$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)} \qquad \Delta H = +787\ kJ\ mol^{-1}$$

Born Haber Cycle

The energy change in a cyclic process is always zero. It finds its application in Hess's law.

Purpose

It is used to calculate lattice energy of binary ionic compounds like M^+X^-.

Lattice energy

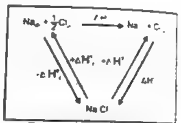
"The enthalpy of formation of one mole of an ionic compound from its gaseous opposite ions under standard conditions is called lattice energy."

e.g.

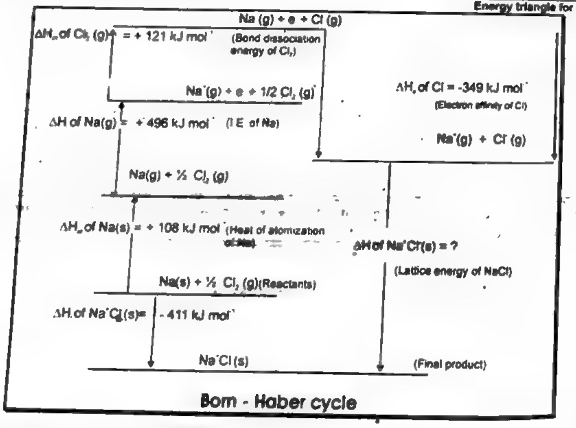
$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow Na^+Cl^-_{(s)} \quad \Delta H^\circ_{Lat} = -787\ kJ\ mol^{-1}$$

Lattice energy cannot be determined directly but values can be obtained indirectly by means of an energy cycle.

Since, ΔH°_f, the standard enthalpy of formation of NaCl, can be measured conveniently in a calorimeter. ΔH°_f can be obtained if ΔH_x which is the total energy involved in changing sodium and chlorine from their normal physical states to gaseous ions, can be calculated.



Energy triangle for NaCl



Born - Haber cycle

It is clear that

$$\Delta H^\circ_f = \Delta H_x + \Delta H^\circ_{lat}$$

$$\Delta H^\circ_{lat} = \Delta H^\circ_f - \Delta H_x$$

$$\Delta H_x = \Delta H_{at(Na)} + \Delta H_{i(Na)} + \Delta H_{at(Cl)} + \Delta H_{e(Cl)}$$

(i) $\Delta H_{at(Na)}$ = ?

The heat of atomization of sodium can be calculated from values of

- Heat of fusion
- Heat of vaporization
- Specific heat capacity

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad \Delta H_{(atm)} = 108\ kJ\ mol^{-1}$$

(ii) $\Delta H_{i(Na)}$ = ?

The first ionization energy of sodium can be obtained spectroscopically

$$Na_{(g)} \longrightarrow Na^+_{(g)} + 1e^- \qquad \Delta H_i = 496\ kJ\ mol^{-1}$$

(iii) $\Delta H_{at(Cl)}$ = ?

The heat of atomization of chlorine can be obtained from spectroscopic studies

$$\tfrac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad \Delta H_{at} = 121\ kJ\ mol^{-1}$$

(iv) $\Delta H_{e(Cl)}$ = ?

The electron affinity of chlorine can also be found by spectroscopic studies.

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H_e = -349\ kJ\ mol^{-1}$$

(v) ΔH_x

Thus

$$\Delta H_x = (108 + 496 + 121 - 349)$$
$$= 376\ kJ\ mol^{-1}$$

Lattice energy of sodium chloride can be obtained.

$$\Delta H_l = \Delta H^\circ_f - \Delta H_x$$

So, $\Delta H_l = -411\ kJ\ mol^{-1} - 376\ kJ\ mol^{-1}$

$$= -787\ kJ\ mol^{-1}$$

The lattice energy gives us the some idea of force of attraction between Na^+ and Cl^- in crystalline solid of sodium chloride.

Advantages of Born Haber Cycle

(i) We calculate lattice energy of ionic compound.
(ii) Lattice energies are very helpful in discussing the structure, bonding and properties of ionic compounds

KEY POINTS

1. Substances exist because they possess energy. Energy can be transformed in the form of heat and the study of heat changes accompanying a chemical reaction is called thermochemistry.
2. Whenever, a reaction happens, then the driving force is the enthalpy change, along with the entropy change Both these parameters decide upon spontaneity of reaction.
3. Most of the thermodynamic parameters are state functions.
4. First law of thermodynamics is the law of conservation of energy and helps us to understand the equivalence of heat and work.

5. When heat is supplied to the system at constant pressure, then is the enthalpy change of the system. Anyhow, at constant volume, the heat supplied is just equal to internal energy change.

6. There is difference between heat and temperature. The amount of heat evolved or absorbed can be measured in laboratory by using glass calorimeter or bomb calorimeter. The amount of heat is calculated from mass of the reactants, specific heat and change of temperature.

7. Hess's law of heat summation is another form of first law of thermodynamics. It helps us to determine the enthalpy changes of those chemical reactions, which cannot be carried out in laboratory or heat changes are difficult to measure.

8. According to Born-Haber cycle (another form of Hess's law) the energy change in a cyclic process is always equal to zero. With the help of this cycle, we can calculate lattice energy of ionic crystals.

SOLVED OBJECTIVE EXERCISE

Q1. Select the suitable answer from given choices:

(i) If an endothermic reaction is allowed to take place very rapidly in the air, the temperature of the surrounding air
- (a) remains constant
- (b) Increases
- (c) Decreases
- (d) remains unchanged

(ii) In endothermic reactions, the heat contents of:
- (a) product is more than that of reactants
- (b) reactant is more than that of product
- (c) both (a) and (b)
- (d) reactants and products are equal

(iii) Calorie is equivalent to:
- (a) 0.4184 J
- (b) 41.84 J
- (c) 4.184 J
- (d) 418.4 J

(iv) The change in heat energy of a chemical reaction at constant temperature and pressure is called:
- (a) enthalpy change
- (b) heat of sublimation
- (c) bond energy
- (d) internal energy change

(v) Which of the following statements is contrary to the first law of thermodynamics?
- (a) energy can neither be created nor destroyed
- (b) one form of energy can be transformed into an equivalent amount of other kinds of energy
- (c) in an adiabatic process, the work done is independent of its path
- (d) continuous productions of mechanical work without supplying an equivalent amount of heat is possible

(vi) For a given process, the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to each other as:
- (a) $q_p = q_v$
- (b) $q_p < q_v$
- (c) $q_p > q_v$
- (d) $q_p = q_v/2$

(vii) For a given reaction $NaOH + HCl \longrightarrow NaCl + H_2O$ the change in enthalpy is called:
- (a) heat of reaction
- (b) heat of formation
- (c) heat of neutralization
- (d) heat of combustion

(viii) The net heat change in a chemical reaction is same whether it is brought about in two or more different ways in one or several steps. It is known as:
- (a) Henry's Law
- (b) Hess's law
- (c) Joule's principle
- (d) Law of conservation of energy

(ix) Enthalpy of neutralization of all the strong acids and strong bases has the same value because:
- (a) neutralization leads to the formation of salt and water
- (b) strong acids and bases are ionic substances
- (c) acids always give H^+ ions and bases OH^- ions
- (d) the net chemical change involve the combination of H^+ and OH^- to form water

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(c) decreases	In endothermic reaction, a system absorbs energy from its surroundings. If it takes place very rapidly the temperature of surroundings decreases
(ii)	(a) product is more than that of reactants	A substance exists because it possesses energy. If the enthalpy (heat contents) of the reactants is less than that of products, the reaction is endothermic
(iii)	(c) 4.184 J	1 cal = 4.184 J
(iv)	(a) enthalpy change	The change in heat energy of a chemical reaction at constant temperature and pressure is called enthalpy change (ΔH)
(v)	(d) continuous productions of mechanical work without supplying an equivalent amount of heat is possible	According to first law of thermodynamics "Energy can neither be created nor destroyed during a chemical reaction but can be changed from one form to another." or "The total energy of a system and its surroundings remain constant." It is also called law of conservation of energy
(vi)	(c) $q_p > q_v$	Since more amount of energy is required when a reaction is carried out at constant pressure than at constant volume so $q_p > q_v$
(vii)	(c) heat of neutralization	The reaction between an acid and a base is a neutralization reaction and heat evolved is called heat of neutralization.
(viii)	(b) Hess's law	According to Hess's law: "If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same."
(ix)	(d) the net chemical change involve the combination of H^+ and OH^- to form water	Enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components. $H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$ $H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} \quad \Delta H^\circ_n = -57.4\ kJ\ mol^{-1}$

Q2. Fill in the blanks with suitable words:

(i) The substance undergoing a physical or a chemical change forms a chemical __________.

(ii) The change in internal energy __________ be measured.

(iii) Solids which have more than one crystalline forms possess __________ values of heat of formation

(iv) A process is called __________ if it takes place on its own without any external assistance.

(v) A __________ is a macroscopic property of system which is __________ of the path adopted to bring about that change.

ANSWERS

(i) system	(ii) can
(iii) different	(iv) spontaneous
(v) State function, independent	

Q3. Indicate the true or false as the case may be:

(i) It is necessary that a spontaneous reaction should be exothermic.

(ii) Amount of heat absorbed at constant volume is internal energy change.

(iii) The work done by the system is given the positive sign.

(iv) Enthalpy is a state function but internal energy is not.
(v) Total heat contents of a system in called enthalpy of system.

ANSWERS

(i) False	(ii) True	(iii) False	(iv) False	(v) True

SHORT ANSWERS TO EXERCISE

Q5a. Differentiate between the following:

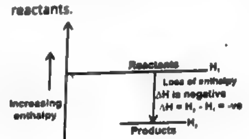
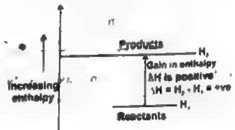
(i) Internal energy and enthalpy

Internal Energy	Enthalpy
1. The total of all the possible kinds of energies of the system is called internal energy.	1. The total heat contents of a system which is a sum of internal energy and product of pressure and volume is called enthalpy.
2. Mathematically $E = K.E. + P.E.$	2. Mathematically $H = E + PV$
3. For a given system, the value of E is smaller than H by a factor PV $E = H - PV$	3. For a given system, the value of H is greater than E by a factor PV. $H = E + PV$

(ii) Internal energy change and enthalpy change

Internal Energy change (ΔE)	Enthalpy change (ΔH)
1. The internal energy change of a chemical reaction is equal to the heat absorbed or evolved by a system at constant volume.	1. The enthalpy change of a chemical reaction is equal to the heat absorbed or evolved by a system at constant pressure.
2. $\Delta E = q_v$	2. $\Delta H = q_p$
3. $\Delta E = E_2 - E_1$	3. $\Delta H = H_2 - H_1$
4. $\Delta E = \Delta H - P\Delta V$	4. $\Delta H = \Delta E + P\Delta V$

(iii) Exothermic reaction and Endothermic reaction

Exothermic reaction	Endothermic reaction
1. In this reaction, heat is evolved from the system.	1. In this reaction, heat is absorbed by the system.
2. The heat contents of product is less than that of reactants. 	2. The heat contents of products is more than that of reactants. 

Exothermic reaction	Endothermic reaction
3. ΔH is negative.	3. ΔH is positive.
4. The Number of bonds formed is greater than the bonds breakage during a reaction.	4. The number of bond breakage is greater than the bonds formation during a reaction.
5. The temperature of the system rises and eventually heat flows from system to surroundings.	5. The temperature of the system falls and eventually heat flows from surroundings to system.
6. The most spontaneous reactions are exothermic.	6. The most non-spontaneous reactions are endothermic.
Example $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7\ kJ\ mol^{-1}$	Examples $N_{2(g)} + O_{2(g)} \longrightarrow NO_{(g)}$ $\Delta H = 180\ kJ\ mol^{-1}$

Spontaneous reaction	Non-spontaneous reaction
1. A reaction which takes place on its own without any external assistance and moves from a non-equilibrium state to equilibrium state is called spontaneous.	1. A reaction which does not take place on its own and needs external assistance to carry out is called non-spontaneous reaction.
2. It is a unidirectional reaction.	2. It can be reversed.
3. It is a real process (natural process).	3. It does not occur in nature (usually).
4. Example (i) $NaOH + HCl \longrightarrow NaCl + H_2O$ (ii) $CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$ (iii) The flow of water down hill (iv) The burning of candle. (v) The flow of heat from hotter to colder body.	5. Example (i) Pumping water uphill. (ii) The flow of heat from colder part of refrigerator to hotter surroundings. (iii) The reaction of $N_2 + O_2$ (natural) during lightning and thunder storm. $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ $\Delta H = 180\ kJ\ mol^{-1}$

Q8. What is the difference between heat and temperature? Write a mathematical relationship between these two parameters.

Heat	Temperature
1. The total kinetic energy of all the molecules of a substance is called heat.	1. The average kinetic energy of all molecules of a substance is called its absolute temperature.
2. It is denoted by 'q'.	2. It is denoted by 'T'.
3. It is not a state function and just a way to transfer energy.	3. It is a state function.
4. Heat absorbed or evolved can be measured by using glass or bomb calorimeter.	4. Temperature is measured by a thermometer.
5. Unit for heat is joules, $kJ\ mol^{-1}$, $cal\ mol^{-1}$.	5. Unit for temperature is °C, °F or Kelvin.
6. It depends upon the quantity of substance.	6. It is independent of the quantity of a substance.

Mathematically $q = m \times s \times \Delta T$

or $q = c \times \Delta T$

where q = heat absorbed/evolved

m = mass of substance
s = specific heat
ΔT = change in temperature
c = heat capacity if mass is one gram

Q9. Define heat of neutralization. When a dilute solution of a strong acid is neutralized by a dilute solution of a strong base the heat of neutralization is found to be nearly the same? How do you account for this?

Ans. "Enthalpy of neutralization is the amount of heat evolved when one mole of hydrogen ions H^+ from an acid react with one mole of hydroxide OH^- ions from a base to form one mole of water.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \qquad \Delta H = -57.4\ kJ\ mol^{-1}$$

All strong acids and bases ionize completely in aqueous solutions providing equal number of H^+ and OH^- ions depending upon concentration of solutions.

So a net result of neutralization is just the formation of water from its ionic components.

For all strong acids and bases with equimolar concentrations of ions, the value of heat of neutralization is same i.e., $-57.4\ kJ\ mol^{-1}$ or $13.2\ Kcal\ mol^{-1}$.

Q10a. State the laws of thermochemistry and show how are they based on the first law of thermodynamics?

Ans. 1st law of thermodynamics is law of conservation of energy. It is stated that

"Energy can neither be created nor be destroyed but can change from one form to another."

There are two important thermo chemical laws which are based on law of conservation of energy i.e.,

(i) 1st law of thermochemistry.
(ii) 2nd law of thermochemistry or Hess's law.

1st law of thermo chemistry: "The amount of heat required to decompose a compound into its element is equal to the amount of heat evolved when that compound is formed from its elements".

Example

$$Na^{1+}_{(g)} + Cl^{1-}_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H_{Lattice} = -787\ kJmol^{-1}$$
$$NaCl_{(s)} \longrightarrow Na^{1+}_{(g)} + Cl^{1-}_{(g)} \qquad \Delta H_{Lattice} = +787\ kJmol^{-1}$$

It is in accordance with law of conservation of energy.

2nd law of thermochemistry/Hess's law: "The amount of heat evolved or absorbed in a process including a chemical change is same wether the process takes place in one step or several steps."

Mathematically,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 .....$$

Enthalpy of direct route = Sum of enthalpies of indirect route

or

"The enthalpy change of a system depends upon its initial and final stage only. It is independent of the path followed by system".

or

"Sum of enthalpies of a cyclic process is zero".

$$\Sigma H_{cycle} = 0$$

It also satisfies the law of conservation of energy.

Q10b. What is a thermochemical equation? Give three examples. What information do they convey?

Ans. **Definition:** A balanced chemical equation which fully describes the physical states of reactants and products in the form of state symbols along with an enthalpy change during the reaction is called a **thermochemical equation.**

Information from thermo chemical equation: It tells us about

(i) Physical states of both reactants and products.
(ii) Exact number of moles of reactants and products.
(iii) Heat evolved or absorbed during a reaction

Examples:

(i) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \qquad \Delta H = -285.8\ kJ\ mol^{-1}$
(ii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -393.7\ kJ\ mol^{-1}$
(iii) $\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H = +218\ kJ\ mol^{-1}$

Q10c. Why is it necessary to mention the physical states of reactants and products in a thermo chemical reaction? Apply Hess's law to justify your answer?

Ans. It is necessary to mention the physical state of reactants and products, because enthalpy is associated with a typical phase of a substance. With a change in physical state of reactants or products, enthalpy change of the reaction will be changed.

So apparently two reactions are chemically same but thermo chemically, they may be different from each other

Application of Hess's law: Steam is produced from H_2 and O_2 by two different routes.

Route I:

(i) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)} \quad \Delta H = -241.5\ kJ\ mol^{-1}$

Route II:

(ii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H_1 = -285.8\ kJ\ mol^{-1}$
(iii) $H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H_2 = +44.3\ kJ\ mol^{-1}$

According to Hess's law

$\Delta H = \Delta H_1 + \Delta H_2$

$-241.5 = (44.3) + (-285.8) = -241.5$

So Hess's law is only proved by thermochemical equations.

Q20. What is the meaning of term enthalpy of ionization?

Ans. "Energy absorbed during the process of ionization is called enthalpy of ionization."

Reason: Weak electrolytes do not completely ionize in water as their molecular forms are stable. So heat energy is required to ionize weak electrolyte in their aqueous solution which is enthalpy of ionization

Example

$$CH_3COOH_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)} \qquad \Delta H = +2.1\ kJ\ mol^{-1}$$

Numericals of Exercise

Q13. $50cm^3$ of 1.0M HCl is mixed with $50cm^3$ of 1.00M NaOH in a glass calorimeter. The temperature of the resultant mixture increases from 21.0°C to 27.5°C. Assume that calorimeter losses are negligible. Calculate the enthalpy change mole^{-1} for the reactions. The density of solution to be considered is $1gcm^3$ and specific heat is $4.18\ Jg^{-1}\ K^{-1}$.

Ans. **Given data**

Volume of HCl = $50.00\ cm^3$
Molarity of HCl = 1.0

Volume of NaOH	=	$50.00\ cm^3$
Molarity of NaOH	=	1.00
Initial tempertature	=	21.0°C
Final temperature	=	27.5°C
Density of solution	=	$1.00\ mg\ cm^{-3}$
Specific heat of solution	=	$4.18\ Jk^{-1}\ g^{-1}$
Total volume of solution	=	$50 + 50 = 100\ cm^3$
Density of solution	=	$1.0\ g\ cm^{-3}$
Enthalpy change	=	?

First of all calculate mass of solution

Formula applied:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

Mass of solution = volume × density

Putting values

Mass of solution = $100\ cm^3 \times 1.00\ g\ cm^{-3}$

Mass of solution = 100 g

Change of temperature (T) = 27.5°C – 21.00°C

= 6,5 C° = 6.5 K

Since temperature has increased, so the reaction is exothermic.

Formula applied:

q = $-s \times m \times \Delta t$

Putting the values

q = $-4.18\ kJ^{-1}\ K^{-1} \times (100g) \times (6.5\ K)$

q = $-2700\ J = -2.7\ kJ$

This is the amount of heat when $50\ cm^3$ of HCl and $50\ cm^3$ of NaOH react to neutralize each other with molarity of 1.00.

Enthalpy change on molar basis:

It is a fact that the number of moles of HCl and NaOH are given by the product of respective solution in dm^3 and their concentrations.

Vol. of HCl in $dm^3 = \frac{50\ cm^3}{1000}$ = $0.05\ cm^3$

Concentration of HCl = $1\ mol\ dm^{-3}$

So, number of moles of HCl = $0.05\ dm^3 \times 1\ mol\ dm^{-3}$

= 0.05

Similarly, the number of moles of NaOH = $0.05\ dm^3 \times 1\ mole\ dm^{-3}$

= 0.05

0.05 moles of each HCl and NaOH evolves heat = –2.7 kJ

1 moles of each HCl and NaOH evolves heat = $\frac{-2.7}{0.05}$ kJ

= – 54 kJ

So, heat of neutralization is = $-54\ kJ\ mol^{-1}$

Q14. Hydrazine N_2H_4 is a rocket fuel. It burns in oxygen to give N_2 and H_2O.

$$N_2H_{4(l)} + O_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$$

1.0 g of N_2H_4 is burnt in bomb calorimeter. An increase of temperature 3.51°C is recorded. Heat capacity of calorimeter is 5.5 kJ k^{-1}. Calculate the quantity of heat evolved. Also, calculate the heat of combustion of 1 mol of N_2H_4.

Ans. Given data:

Mass of N_2H_4 = m = 1 g

Heat capacity = c = $5.5\ kJ\ K^{-1}g^{-1}$

ΔT = $T_2 - T_1$ = 3.51°C = 3.51 K

Requirement:

(i) Quantity of heat for 1 g = q = ?

Quantity of heat for 1 mole = q = ?

Solution:

(i) q = $c\Delta T$ [when m = 1 g]

q = $5.5\ kJ\ K^{-1} \times 3.51\ K$

(Since heat is evolved so negative sign is used)

q = –19.3 kJ

(ii) **To calculate heat evolved by one mole,**

Molar mass of N_2H_4 = $(14 \times 2) + (1 \times 4)$

= $28 + 4 = 32\ g\ mol^{-1}$

As in 1st step .

The amount of heat evolved when 1 gram of N_2H_4 is burnt = –19.3 kJ

The amount of heat evolved when 32 gram N_2H_4 is burnt = $-19.3\ kJ \times 32\ g\ mol^{-}$

= $-617.76\ kJ\ mol^{-1}$

(i) Quantity of heat for 1 g = –19.3 kJ

(ii) Quantity of heat for 1 mol = $-617.76\ kJ\ mol^{-1}$

Q15. Octane C_8H_{18} is a motor fuel. 1.80g of a sample of octane is burned in a bomb calorimeter having heat capacity 11.66 kJK^{-1}. The temperature of the calorimeter increases 21.36°C to 28.78°C. Calculate the heat of combustion for 1g of octane. Also calculate the heat for 1 mole of octane.

Ans. Given data

Mass of octane burnt	=	1.8g
Heat capacity of calorimeter	=	$11.66\ kJ\ K^{-1}$
Initial temperature	=	21.36 C°
Final temperature	=	28.78 C°
Rise of temperature	=	28.78 – 21.36
	=	7.42 C° = 7.42 K
Heat of combustion	=	?

Formula applied:

Putting the values

q = $-m \times s \times \Delta t$

q = $-1.8\ g \times 11.6\ kJ\ K^{-1} \times 7.42\ K$

q = $-155.73\ kJ\ g$

Amount of heat evolved for 1 g of octane

= $\frac{-155.73\ kJ\ g^{-1}}{1.8g}$

	=	-86.51 kJ
Molar mass of octane	=	$12 \times 8 + 1 \times 18 = 96 + 18$
	=	$114\ g\ mol^{-1}$
Amount of heat evolved for 1 mole of octane		
	=	-86.51×114
	=	$-9862.14\ kJ\ mole^{-1}$

Q16. By applying Hess's law, calculate the enthalpy change for the formation of an aqueous solution of NH_4Cl from NH_3 gas and gas HCl. The results for the various reactions are as follows:

Ans. Given data:

(i) $NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\quad \Delta H_1 = -35.16\ kJ\ mol^{-1}$

(ii) $HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\quad \Delta H_2 = -72.41\ kJ\ mol^{-1}$

(iii) $NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\quad \Delta H_3 = -51.48\ kJ\ mol^{-1}$

Requirement:

$$NH_{3(g)} + HCl_{(g)} + aq \longrightarrow NH_4Cl_{(aq)} \quad \Delta H_f = ?$$

Solution:

To get the required equation from the given data, added up equations i, ii and iii.

(i) $NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\quad \Delta H_1 = -35.16\ kJ\ mol^{-1}$

(ii) $HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\quad \Delta H_2 = -72.41\ kJ\ mol^{-1}$

(iii) $NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\quad \Delta H_3 = -51.48\ kJ\ mol^{-1}$

$NH_{3(g)} + HCl_{(g)} + aq \longrightarrow NH_4Cl_{(aq)}$ $\quad \Delta H_f = -159.09\ kJ\ mol^{-1}$

Enthalpy of formation of $NH_4Cl = -159.09\ kJ\ mol^{-1}$

Q17. Calculate the heat of formation of ethyl alcohol from the following information.

Ans. Given data:

(i) Heat of combustion of ethyl alcohol:

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \quad \Delta H = -1367\ kJ\ mol^{-1}$$

(ii) Heat of formation of CO_2:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.7\ kJ\ mol^{-1}$$

(iii) Heat of formation of H_2O:

$$H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H = -285.8\ kJ\ mol^{-1}$$

Requirement:

Heat of formation of ethyl alcohol = ?

$$2C_{(s)} + 3H_{2(g)} + 1/2O_{2(g)} \longrightarrow C_2H_5OH_{(l)} \quad \Delta H_f = ?$$

Solution:

To get the required equation, multiply equation (ii) with 2 and equation (iii) with 3 and added them

(ii) $2C_{(s)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)}$ $\quad \Delta H = -393.7 \times 2 = -787.4\ kJ\ mol^{-1}$

(iii) $3H_{2(g)} + 3/2O_{2(g)} \longrightarrow 3\ H_2O_{(l)}$ $\quad \Delta H = -285.8 \times 3 = -857.4\ kJ\ mol^{-1}$

(iv) $2C_{(s)} + 3H_{2(g)} + 7/2O_{2(g)} \longrightarrow 2CO_{2(g)} + 3\ H_2O_{(l)}$ $\quad \Delta H = -1644.8\ kJ\ mol^{-1}$

Now invert the equation (i) and add it into equation (iv) along with their enthalpies.

(i) $2CO_{2(g)} + 3H_2O_{(l)} \longrightarrow C_2H_5OH_{(l)} + 3O_{2(g)}$ $\quad \Delta H = +1367\ kJ\ mol^{-1}$

(iv) $2C_{(s)} + 3H_{2(g)} + 7/2O_{2(g)} \longrightarrow 2CO_{2(g)} + 3\ H_2O_{(l)}$ $\quad \Delta H = -1644.8\ kJ\ mol^{-1}$

$2C_{(s)} + 3H_{2(g)} + ½O_{2(g)} \longrightarrow C_2H_5OH_{(l)}$ $\quad \Delta H_f = -277.8\ kJ\ mol^{-1}$

Thus the heat of formation of ethyl alcohol = $-277.8\ kJ\ mol^{-1}$

Q18. If the heats of combustion of C_2H_2, H_2 and C_2H_6 are -337.2, -68.3, -372.8 k calories respectively, then calculate the heat of the following reaction.

$$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)} \quad \Delta H_r = ?$$

Ans. Given data:

(i) $C_2H_{2(g)} + 5/2O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(g)}$ $\quad \Delta H = -337.2\ kcal\ mol^{-1}$

(ii) $H_{2(g)} + ½O_{2(g)} \longrightarrow H_2O_{(l)}$ $\quad \Delta H = -68.3\ kcal\ mol^{-1}$

(iii) $C_2H_{6(g)} + 7/2O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\quad \Delta H = -372.8\ kcal\ mol^{-1}$

Requirement:

$$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)} \quad \Delta H_r = ?$$

Solution:

To get the required equation, in first step multiply equation (ii) with 2 and add it in equation (i) along with their enthalpies.

(i) $C_2H_{2(g)} + 5/2O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(l)}$ $\quad \Delta H = -337.2\ kcal\ mol^{-1}$

(ii) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\quad \Delta H = -68.3 \times 2 = -136.6\ kcal\ mol^{-1}$

(iv) $C_2H_{2(g)} + 2H_{2(g)}\ 7/2O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\quad \Delta H = -473.8\ kcal\ mol^{-1}$

In second step, invert equation (iii) and add it in equation (iv) along with their enthalpies.

(iv) $C_2H_{2(g)} + 2H_{2(g)}\ 7/2O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\quad \Delta H = -473.8\ kcal\ mol^{-1}$

(iii) $2CO_{2(g)} + 3H_2O_{(l)} \longrightarrow C_2H_{6(g)} + 7/2O_{2(g)}$ $\quad \Delta H = +372.8\ kcal\ mol^{-1}$

$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$ $\quad \Delta H_r = -101\ kcal\ mol^{-1}$

Thus the Enthalpy of formation of $C_2H_6 = -101\ kcal\ mol^{-1}$

Q19. Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25°C is $-393.51\ kJ\ mol^{-1}$ and that of diamond is $-395.41\ kJ\ mol^{-1}$. What is the enthalpy change of the process? Graphite $\longrightarrow$ Diamond at the same temperature.

Ans. Given data:

(i) $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H = -393.51\ kJ\ mol^{-1}$

(ii) $C_{(diamond)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H = -395.41\ kJ\ mol^{-1}$

Requirement:

$$C_{(graphite)} \longrightarrow C_{(diamond)} \quad \Delta H = ?$$

Solution:

To obtain the required equation, equation (ii) is inverted and then add it in equation (i):

(i) $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H = -393.51\ kJ\ mol^{-1}$

(ii) $CO_{2(g)} \longrightarrow O_{2(g)} + C_{(diamond)}$ $\quad \Delta H = +395.41\ kJ\ mol^{-1}$

$C_{(graphite)} \longrightarrow C_{(diamond)}$ $\quad \Delta H = +1.9\ kJ\ mol^{-1}$

Thus the enthalpy change of graphite $\rightarrow$ diamond = $1.9\ kJ\ mol^{-1}$

Q20. If heat of neutralization of HCl and NaOH is –57.3 kJ mol⁻¹ and heat of neutralization of CH_3COOH with NaOH is –55.2 kJ mol⁻¹, calculate enthalpy of ionization of CH_3COOH?

Ans. Given data:

(i) $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ $\quad \Delta H = -57.3\ kJ\ mol^{-1}$

(ii) $CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + CH_3COO^-_{(aq)}$ $\quad \Delta H = -55.2\ kJ\ mol^{-1}$

Requirement:

$CH_3COOH_{(aq)} \rightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$ $\quad \Delta H = ?$

Solution:

To obtain the required equation invert the equation (i) and then add it in equation (ii):

(i) $H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$ $\quad \Delta H = +57.3\ kJ\ mol^{-1}$

(ii) $CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + CH_3COO^-_{(aq)}$ $\quad \Delta H = -55.2\ kJ\ mol^{-1}$

$CH_3COOH_{(aq)} \longrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$ $\quad \Delta H = 2.1\ kJ\ mol^{-1}$

Thus the enthalpy of ionization of $CH_3COOH = 2.1\ kJ\ mol^{-1}$

Q21c. Using the information given below, calculate lattice energy of potassium bromide KBr.

Ans. Given data:

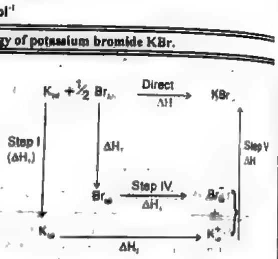
(i) $K_{(s)} + \frac{1}{2}Br_{2(l)} \longrightarrow KBr_{(s)}$ $\quad \Delta H = -392\ kJ\ mol^{-1}$

(ii) $K_{(s)} \longrightarrow K_{(g)}$ $\quad \Delta H = +90\ kJ\ mol^{-1}$

(iii) $K_{(g)} \longrightarrow K^{+1}_{(g)} + e^-$ $\quad \Delta H = 420\ kJ\ mol^{-1}$

(iv) $\frac{1}{2}Br_{2(l)} \longrightarrow Br_{(g)}$ $\quad \Delta H = 112\ kJ\ mol^{-1}$

(v) $Br_{(g)} + e^- \longrightarrow Br^-_{(g)}$ $\quad \Delta H = -342\ kJ\ mol^{-1}$



Requirement:

$K^+_{(g)} + Br^-_{(g)} \rightarrow KBr$ $\quad \Delta H_{lattice} = ?$

Solution:

The equation (i) shows the enthalpy of formation of potassium bromide. According to Hess's law the enthalpy of formations is equal to sum of all the enthalpies along with lattice energy.

$\Delta H_f = \Delta H_{lattice} + \Delta H_x$

$\Delta H_{lattice} = \Delta H_f - \Delta H_x$

Where ΔH_x is equal to some of all the given enthalpies to get ΔH_x add equations (ii), (iii), (iv) and (v).

(ii) $K_{(s)} \longrightarrow K_{(g)}$ $\quad \Delta H = +90\ kJ\ mol^{-1}$

(iii) $K_{(g)} \longrightarrow K^{+1}_{(g)} + e^-$ $\quad \Delta H = 420\ kJ\ mol^{-1}$

(iv) $\frac{1}{2}Br_{2(l)} \longrightarrow Br_{(g)}$ $\quad \Delta H = 112\ kJ\ mol^{-1}$

(v) $Br_{(g)} + e^- \longrightarrow Br^-_{(g)}$ $\quad \Delta H = -342\ kJ\ mol^{-1}$

$K_{(s)} + \frac{1}{2}Br_{2(l)} \longrightarrow K^{+1}_{(g)} + Br^-_{(g)}$ $\quad \Delta H_x = -280\ kJ\ mol^{-1}$

$\Delta H_{lattice} = \Delta H_f - \Delta H_x$

$\Delta H_{lattice} = -392 - 280$

$\Delta H_{lattice} = -672\ kJ\ mol^{-1}$

Thus the lattice energy of potassium bromide = –672 kJ mol⁻¹

SOLVED EXAMPLES

Example 1:

When 2.00 moles of H_2 and 1.00 mole of O_2 at 100°C and 1 torr pressure react to produce 2.00 moles of gaseous water, 484.5 kJ of energy are evolved. What are the values of (a) ΔH (b) ΔE for the production of one mole of H_2O (g)?

Solution:

(a) The reaction is occurring at constant pressure.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

The enthalpy change for one mole of water vapours is

$$\Delta H = \frac{-484.5kJ}{2\ \text{moles of}\ H_2O} = -242.2kJ\ mol^{-1}$$

The minus sign shows that the reaction is exothermic for the production of 1 mole of water.

(b) To calculate ΔE from ΔH, we use the equation (4)

$\Delta H = \Delta E + P\Delta V$

Let us, first calculate the value of PDV using the ideal gas equation

$PV = nRT$

Or $P\Delta V = \Delta nRT$

Now, Δn = No. of moles of the products – No. of moles of the reactants

= 2 moles – 3 moles = -1 mole

$R = 8.314J\ K^{-1}\ mol^{-1}$

$T = 373\ K$

$P\Delta V = \Delta nRT$ .... (6)

$P\Delta V = -1\ mole \times 8.314J\ mol\ K^{-1} \times 373\ K$

$P\Delta V = -3100J = -3.10kJ$

This is the value of 2 moles of water. For the formation of 1 mole of 2ater,

$$P\Delta V = \frac{-3.10}{2} = -1.55kJ\ mol^{-1}$$

On substituting, these vales into equation (4).

$\Delta H = \Delta E + P\Delta V$

$\Delta E = \Delta H - P\Delta V$

$= -242.2 - (-1.55) = -242.2 + 1.55$

$\Delta E = -240.6kJ\ mol^{-1}$

Example 2:

Neutralization of 100 cm³ of 0.5 M NaOH at 25°C with 100 cm³ of 0.5M HCl at 25°C raised the temperature of the reaction mixture to 28.5°C. Find the enthalpy of neutralization. Specific heat of water 4.2J K⁻¹ g⁻¹

Solution:

Specific heat of water, s = 4.2 JK⁻¹ g⁻¹

Density of H_2O is around 1 gcm⁻³, so 200 cm³ of total [illegible] approximately = 200 g

Hence, total mass of the reaction mixture = 200 g

Rise in temperature, ΔT = 28.5 – 25.0 = 3.5°C = 3.5K

$100cm^3$ of 0.5M NaOH = $100cm^3$ of 0.5 M HCl

0.5 m solution means that 1000 cm^3 of solution has 0.5 moles of solute

So $100cm^3$ of 0.5 M solution = 0.05 moles of HCl and NaOH, respectively

Amount of total heat evolved, (q) $= m \times s \times \Delta T$

$= 200g \times 4.2Jg^{-1}K^{-1} \times 3.5K = 2940J$

$= 2940J = 2.94kJ$

Since, the reaction is exothermic

So, q = 1 − 2.94kJ

When this heat is divided by number of moles, then ΔH_n° is for one mole

Enthalpy of neutralization, $(\Delta H^\circ_n) = \dfrac{-2.94kJ}{0.05mol} = -58.8kJ\ mol^{-1}$

Example (3):

10.16g of graphite is burnt in a bomb calorimeter and the temperature rise recorded is 3.87K. Calculate the enthalpy of combustion of graphite, if he heat capacity of the calorimeter (bomb, water, etc.) is 86.02kJK^{-1}

Ans. Given Data:

Heat capacity of bomb calorimeter = $86.02kJK^{-1}$

Rise in temperature = ΔT = 3.87K

Mass of graphite = m = 10.6gram

Required:

Enthalpy of combustion = ΔH_c° = ?

Solution:

Heat gained $= q = c \times \Delta T$

$= 86.02kJK^{-1} \times 3.87K$

$= 332.87kJ$

This heat is evolved by burning 10.6g of graphite.

Number of mole of graphite $= \dfrac{\text{Mass of graphite}}{\text{Atomic mass of graphite}}$

$= \dfrac{10.6g}{12g\,mol^{-1}} = 0.843\ mol$

Hence, enthalpy of combustion of graphite per mole $= \dfrac{332.89kJ}{0.843mol}$

$= 395kJmol^{-1}$

Since heat is evolved during combustion, so the sign of the answer would be negative

$\Delta H_c^\circ = -395kJ\ mol^{-1}$

Important Previous Board Questions

Q. How do we determine the ΔH in the laboratory for food, fuel etc.?

Q. Justify that heat of formation of compounds is sum of all the other enthalpies.

Q. The total energy of a system is the sum of translational, rotational and vibrational motions. Justify it.

For Answers study Scholar's CHEMISTRY (Objective) XI

Chapter 8

CHEMICAL EQUILIBRIUM

Reversible Reaction

"A chemical reaction in which products of a reaction can react to form the original reactants under the same set of conditions is called a reversible reaction."

or

"A chemical reaction which takes place in both directions i.e. forward and reverse under same conditions is called reversible reaction."

$$\underset{\text{Reactants}}{A + B} \rightleftharpoons \underset{\text{Products}}{C + D}$$

Representation

It is represented by writing a double arrow ($\rightleftharpoons$) between reactants and products.

Important points

- A reversible reaction can never go to completion.
- Usually, it can be carried out in a closed vessel.
- In reversible reaction, equilibrium state is the ultimate goal/fate.

Examples

1. $H_{2(g)} + I_{2(g)} \xrightleftharpoons{425^\circ C} 2HI_{(g)}$
2. $N_{2(g)} + 3H_{2(g)} \xrightleftharpoons[\text{High Pressure}]{Fe/450^\circ C} 2NH_{3(g)}$
3. $CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \xrightleftharpoons{H^+} CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$

Q4. (a) Explain the terms "reversible reaction" and "state of equilibrium."

Irreversible Reaction

"A chemical reaction in which products of the reaction do not react to form the original reactants under same conditions is called irreversible reaction."

or

"A chemical reaction which takes place in one direction only under same conditions is called irreversible reaction."

$$\underset{\text{Reactants}}{A + B} \longrightarrow \underset{\text{Products}}{C + D}$$

Representation

It can be represented by an arrow ($\longrightarrow$) from reactants to products.

Important points

- In irreversible reaction, the reaction goes to almost completion.
- There is no sign of equilibrium state.
- It can be carried out in open or closed vessel.

Examples

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

$$2H_{2(g)} + O_{2(g)} \xrightarrow[\text{Discharge}]{\text{Electric Spark}} 2H_2O_{(l)}$$

State of Chemical Equilibrium (Equilibrium State)

"A state achieved by reversible chemical reaction in which the forward and reverse processes are occurring at the same rate is called state of chemical equilibrium or equilibrium state."

Characteristics of equilibrium state

(i) When the equilibrium state is established at a constant temperature, the concentration (amount) of reactants and products becomes constant.

(ii) The equilibrium state can be achieved from either direction.

(iii) The equilibrium state cannot be attained in an open vessel.

(iv) The value of equilibrium constant (K_c) does not depend upon initial concentration of reactants.

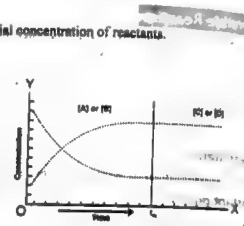
(v) A catalyst does not change the equilibrium state of a reaction.

Reversible reaction and state of equilibrium

Let us consider a general reaction to produce C and D.

$$A + B \rightleftharpoons C + D$$

Suppose that all the substances are in gaseous state. Let the initial concentrations of A and B be equal. As time goes on, concentrations of A and B decrease, at first quite rapidly but later slowly. Eventually, the concentrations of A and B level off and become constant. The graph is plotted between time and concentrations for reactants and products.



Reversible reaction and state of equilibrium

The initial concentration of C and D are zero. As time passes the products C and D are formed. Their concentrations increase rapidly at first and then level off. At the time of equilibrium, the concentrations become constant.

Example

Consider the example of a reversible chemical reaction between hydrogen gas and iodine vapours to form hydrogen iodide at 425°C. At equilibrium three components will be present in definite proportions in the reaction mixture.

State of dynamic equilibrium

The equilibrium is established when the rising curve of product HI and the falling curve of reactants $[H_2]$ and $[I_2]$ become parallel to time X-axis.

$$H_{2(g)} + I_{2(g)} \xrightleftharpoons{425°C} 2HI_{(g)}$$

The same equilibrium mixture is obtained irrespective whether the reaction starts by mixing hydrogen and iodine or by decomposition of hydrogen iodide. The situation suggests two possibilities of the state of reaction at equilibrium.

(i) All reactions cease at equilibrium so that the system becomes stationary.

(ii) The forward and reverse reactions are taking place simultaneously at exactly the same rate. It is now universally accepted that the later conditions prevail in a reversible reaction at equilibrium stage of reaction. It is known as the state of dynamic equilibrium.

Q5. (a) Reversible reactions attain the position of equilibrium which is dynamic in nature and not static. Explain it.

Ans. **Reversible reaction**

"Those reactions in which products can reform the original reactants under same experimental conditions are called reversible reactions."

A chemical equilibrium state in a reversible reaction ~~is a state~~ where the rate of forward reaction becomes equal to rate of reverse reaction. This show that at this state both reaction are taking place simultaneously and not stop thus equilibrium is dynamic not static.

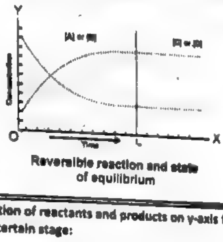
If it would be static all type of reactions would stop.

Q5. (b) Why do rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Ans. (i) According to law of mass action, the rate of reaction is proportional to the products of concentrations of reactants.

As the reactants go on decreasing with the passage of time, the rate of reaction also slows down near the equilibrium.

(ii) In start effective collisions of reactants is greater so a sharp decrease of concentration or steepness of slope of graph is observed. With the formation of products, hindrance is created for effective collisions so rate of reaction is decreased.



Reversible reaction and state of equilibrium

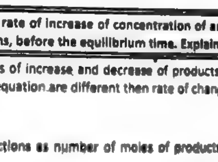
Q6. When a graph is plotted between time on x-axis and the concentration of reactants and products on y-axis for a reversible reaction, the curves becomes parallel to time axis at a certain stage:

(a) At what stage the curve become parallel?

Ans. In a reversible reaction, the concentration of reactants and products become constant at equilibrium stage but the reaction does not stop. Therefore, at the equilibrium stage the curves of the concentration of reactants and products become parallel.

(b) Before the curve become parallel, the steepness of curve falls

Ans. At the beginning of the reversible reactions, the concentration of the reactants decreases and concentration of the product increases rapidly. As a result of this two curve show greater steepness but as reaction approaches to equilibrium stages both rate of forward and reverse reaction become slow according to law of mass action. Due to this, near the equilibrium point the steepness of the curves fall before becoming parallel to x-axis.



Reversible reaction and state of equilibrium

(c) The rate of decrease of concentration of any of the reactants and rate of increase of concentration of any of the products may or may not be equal, for various types of reactions, before the equilibrium time. Explain it.

Ans. When no. of moles of reactants and products are equal, then rates of increase and decrease of products and reactants are equal. But when no. of moles in a balanced chemical equation are different then rate of change of concentration of a species will be different from other. e.g.,

$$N_2O_4 \rightleftharpoons 2NO_2$$

Speed of rising curve is greater than falling curve in the said reactions as number of moles of products are greater than number of moles of reactants.

Q.4 (b) Define and explain the Law of mass action and derive the expression for the equilibrium constant (K_c).

LAW OF MASS ACTION

Introduction

A state of dynamic equilibrium helps to determine the composition of reacting substances and the products at equilibrium. We use the relationship which was derived by C.M.Guldberg and P. Waage in 1864.

Statement

"The rate at which the reaction proceeds is directly proportional to the product of active masses of the reactants."

Active mass

The term active mass represents the concentration in mol dm^{-3} of the reactants and products for a dilute solution

Explanation

Consider a general reaction in which A and B are the reactants and C and D are the products. The reaction is represented by following equation:

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$

The equilibrium concentrations of A, B, C and D are represented in square brackets [A] [B] [C] and [D] respectively. They are expressed in mol dm^{-3}. According to law of mass action, rate of forward reaction is proportional to the product of molar concentrations of A and B.

Rate of forward reaction (R_f) $\propto$ [A] [B]

$$R_f = k_f [A][B]$$

Where k_f is the proportionality constant and is called rate constant for forward reaction.

Similarly, rate of reverse reaction is given by:

Rate of reverse reaction (R_r) $\propto$ [C] [D]

$$R_r = k_r [C][D]$$

Where k_r is proportionality constant and is called rate constant for backward reaction. Remember that C and D are the reactants for backward step.

At equilibrium state.

Rate of forward reaction = Rate of backward reaction

$$R_f = R_r$$

$$k_f[A][B] = k_r[C][D]$$

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$\frac{k_f}{k_r} = K_c$$

$$K_c = \frac{[C][D]}{[A][B]}$$

Definition of K_c

(i) "It is the ratio between rate constant for forward reaction and rate constant for reverse reaction."

or

$$K_c = \frac{\text{Rate constant for forward reaction}}{\text{Rate constant for reverse reaction}} = \frac{k_f}{k_r}$$

(ii) "It is the ratio between product of concentration of products and product of concentration of reactants"

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

For more general equation

$$aA + bB \rightleftharpoons cC + dD$$

where a, b, c and d are coefficient of equation and represent number of moles of reactants and products. They are number of moles of A,B,C and D respectively.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

It shows that the coefficients in the equation appear as exponent of the terms of concentration in the equilibrium constant expression

Units of Equilibrium Constant (K_c)

1. If number of moles of reactants and products are equal, then K_c has no units.

(i) $CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$

1 mol 1 mol 1 mol 1 mol

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\text{mol dm}^{-3}\,.\,\text{mol dm}^{-3}}{\text{mol dm}^{-3}\,.\,\text{mol dm}^{-3}} = \text{no units}$$

(ii) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI$

1 mol 1 mol 2 mol

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3}.\text{mol dm}^{-3})} = \text{no units}$$

2. If the number of moles of reactants and products are not equal.

(i) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

4 mol 2 mol

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]^3} = \text{mol}^{-2}\,\text{dm}^{+6}$$

(ii) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Equilibrium constant for this reaction:

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]}{[\text{mol dm}^{-3}]} = \text{mol dm}^{-3}$$

Q8. (a) Write down K_c for the following reversible reactions. Suppose that the volume of reaction mixture in all the cases is 'V' dm^3 at equilibrium state.

quilibrium Constant Expression For Some Important Reactions

(I) Formation of Ester from an Organic Acid and Alcohol (aqueous phase reaction)

$$\underset{\text{Acetic acid}}{CH_3COOH_{(aq)}} + \underset{\text{Ethyl alcohol}}{C_2H_5OH_{(aq)}} \overset{H_3O^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_{5(aq)}} + \underset{\text{water}}{H_2O_{(l)}}$$

Let us suppose that 'a' moles of CH_3COOH and 'b' moles of C_2H_5OH are initially taken in a vessel in the presence of small amount of a mineral acid as catalyst.

The progress of the reaction can be studied by finding out the concentrations of acetic acid after regular intervals. A very small portion of the reaction mixture is withdrawn and the concentration of acetic acid is determined by titrating it against a standard solution of sodium hydroxide (NaOH). The concentration of acetic acid will decrease until the attainment of state of equilibrium, when it will become constant. At equilibrium stage, 'x' moles of ester and 'x' moles of H_2O are produced. The number of moles of acid and alcohol left behind are 'a-x' moles and 'b-x' moles respectively. If the volume of reaction mixture at equilibrium stage is 'V' dm^3, then

	$CH_3COOH_{(aq)}$	$+\ C_2H_5OH_{(aq)}$	$\rightleftharpoons$	$CH_3COOC_2H_{5(aq)}$	$+\ H_2O_{(l)}$
t = 0 sec,	'a' moles	'b' moles	$\rightleftharpoons$	'o' moles	'o' moles
$t = t_{eq}$	(a-x) mol	(b-x) mol	$\rightleftharpoons$	'x' mol	'x' mol

When number of moles are divided by total volume of the reaction mixture, we get concentration of each species at equilibrium stage in moles dm^{-3}.

$$\left(\frac{a-x}{V}\right)\text{moldm}^{-3} + \left(\frac{b-x}{V}\right)\text{moldm}^{-3} \rightleftharpoons \left(\frac{x}{V}\right)\text{moldm}^{-3} + \left(\frac{x}{V}\right)\text{moldm}^{-3}$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]}$$

$$= \frac{\frac{x}{V}\cdot\frac{x}{V}}{\frac{a-x}{V}\cdot\frac{b-x}{V}}$$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

In this expression of K_c, the factor of volume is cancelled out. So, the change of volume at equilibrium stage does not affect the K_c value or equilibrium position of reaction.

(ii) Dissociation of PCl_5 (gaseous phase reaction)

The dissociation of PCl_5 into PCl_3 and Cl_2 is a well-known homogeneous gaseous phase reaction. This reaction has unequal number of moles of reactants and products.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Let 'a' moles of PCl_5 present initially are decomposed by 'x' moles. So, at equilibrium stage.

'a-x' moles of PCl_5 are left behind while 'x' moles of PCl_3 and 'x' moles of Cl_2 are produced. If the volume of equilibrium mixture is 'V' dm^3, then

	$PCl_{5(g)}$	$\rightleftharpoons$	$PCl_{3(g)}$	+	$Cl_{2(g)}$
$t = 0$ sec	'a' moles		'0' moles		'0' moles
$t = t_{eq}$	(a-x) moles		'x' moles		'x' moles

Dividing the number of moles by total volume of reactants and products at equilibrium

$$\left(\frac{a-x}{V}\right) mol\ dm^{-3} \rightleftharpoons \left(\frac{x}{V}\right) mol\ dm^{-3}\ \left(\frac{x}{V}\right) mol\ dm^{-3}$$

Since $\qquad K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

$$K_c = \frac{\frac{x}{V}\cdot\frac{x}{V}}{\frac{a-x}{V}}$$

$$K_c = \frac{x^2}{(a-x)V}$$

The final expression depends upon the factor of volume. So, the change of volume at equilibrium stage disturbs the equilibrium position of the reaction.

(iii) Decomposition of N_2O_4 (gaseous phase reaction)

For the decomposition of $N_2O_{4(g)}$, the expression of K_c involves the factor of volume.

	$N_2O_{4(g)}$	$\rightleftharpoons$	$2NO_{2(g)}$
$t = 0$ sec	'a' mol		'0' mol
$t = t_{eq}$	(a - x) mol		2x mol
	$\left(\frac{a-x}{V}\right) mol\ dm^{-3}$		$\left(\frac{2x}{V}\right)^2 mol\ dm^{-3}$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)}$$

$$K_c = \frac{4x^2}{(a-x)V}$$

'a' is the initial number of moles of N_2O_4, 'x' is number of moles of N_2O_4 decomposed and 'V' is total volume of N_2O_4 and NO_2 at equilibrium stage.

(iv) Synthesis of ammonia (gaseous phase reaction)

	$N_{2(g)}$	+	$3H_{2(g)}$	$\rightleftharpoons$	$2NH_{3(g)}$
$t = 0$ sec	'a' mol		'b' mol		'0' mol
$t = t_{eq}$	(a – x) mol		(b – 3x) mol		'2x' mol
	$\left(\frac{a-x}{V}\right) mol\ dm^{-3}$		$\left(\frac{b-3x}{V}\right) mol\ dm^{-3}$		$\left(\frac{2x}{V}\right) mol\ dm^{-3}$

Since, $\qquad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$$K_c = \frac{(2x/V)^2}{(a-x/V)(b-3x/V)^3}$$

$$K_c = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

Where 'a' and 'b' are the initial number of moles of N_2 and H_2 and 'x' is the number of moles of N_2, decomposed at equilibrium stage, 'V' is the total volume of N_2, H_2 and NH_3 at equilibrium. The final expression involves V^2 in the numerator.

Q8. (b) How some reactions are effected by volume at equilibrium stage?

Ans. (i) If reaction mixture is in gaseous state then at equilibrium if volume is changed it will effect the equilibrium

(ii) If numbers of moles of reactants are not equal to number of moles of product then those gaseous reactions are effected by volume change at equilibrium

For Example:

(i) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

(ii) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Relationships between Equilibrium Constants

The expression of equilibrium constants depend upon the concentration units used.

(i) Mostly the concentrations are represented in mol dm^{-3}. Let us consider the following reversible reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{C_C^c\ C_D^d}{C_A^a\ C_B^b}$$

The square brackets represent the concentration of species in moles dm^{-3}. Anyhow, the capital C is also used for molar concentrations.

(ii) In case of gases, the molar concentration of each gas is proportional to its partial pressure. When the concentrations are expressed in terms of partial pressures, the expression of K_p is,

$$K_p = \frac{p_C^c\ p_D^d}{p_A^a\ p_B^b}$$

Here p_A, p_B, p_C and p_D are partial pressures of A, B, C and D respectively at equilibrium position.

(iii) Some other equilibrium constants are as follows:

$$K_n = \frac{n_C^c n_D^d}{n_A^a n_B^b}$$

$$K_x = \frac{X_C^c X_D^d}{X_A^a X_B^b}$$

Relationships between K_c and K_p

As long as the number of moles of products and reactants are equal, the value of K_c and K_p remain the same. Otherwise, the following relationship between K_c and K_p can be derived by using Dalton's law of partial pressure.

$$K_p = K_c (RT)^{\Delta n}$$

Where, Δn = number of moles of products – number of moles of reactants

$$\Delta n = n_P - n_R$$

R = general gas constant

T = absolute temperature

Case 1

If the number of moles of products and reactants are equal i.e. $\Delta n = 0$

Example $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

$n_R = 2$ mol $\quad n_P = 2$ mol

$\Delta n = 0$

$K_p = K_c (RT)^{\Delta n}$

$K_p = K_c$

Those reactions having same number of moles of reactants and products contain equal value for K_p and K_c.

Case 2

If the number of moles of products are greater than reactants i.e. Δn = +ve

Example $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$n_R = 1$ mol $\quad n_P = 2$ mol

$\Delta n = 2 - 1 = 1$ mol

$K_p = K_c (RT)^{\Delta n}$

In this case: $K_p > K_c$

Case 3

If number of moles of products are less than that of reactants i.e. Δn = –ve

Example $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$n_R = 4$ mol $\quad n_P = 2$ mol

$\Delta n = 2 - 4 = -2$ mol

$K_p = K_c (RT)^{\Delta n}$

In this case. $K_p < K_c$

Q7. (a) Give relationship of K_c & K_p for following

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[Products]}{[Reactants]} \quad \text{so} \quad \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$K_p = K_c(RT)^{\Delta n}$

Δn = no. of moles of P – no. of moles of R.

$(c + d) - (a + b) = y$ moles

So $K_p = K_c (RT)^y$

(b) Decide comparative magnitudes of K_p and K_c for

(i) NH_3 synthesis

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$

$K_p = K_c(RT)^{\Delta n}$

$K_p = K_c(RT)^{-2}$ as $[\Delta n = 2 - 4 = -2]$

so Value of $K_p < K_c$

(ii) Dissociation of PCl_5

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

$K_p = K_c(RT)^{\Delta n}$

$K_p = K_c(RT)^1$ as $\Delta n = 2 - 1 = 1$

So value of $K_p > K_c$ as it is obtained by multiplying $K_c \times RT$.

Q8. Explain the following two applications of equilibrium constant. Give examples

(i) Direction of reaction (ii) Extent of reaction

Applications of Equilibrium Constant

1. Direction of Reaction

We know that

$$K_c = \frac{[Products]}{[Reactants]} \quad \text{(for any reaction)}$$

The direction of a chemical reaction at any particular time can be predicted by means of [Products] / [Reactants] ratio, calculated before the reaction attains equilibrium. The value of [Products] / [Reactants] ratio leads to one of the following three possibilities.

(i) If ratio is greater than K_c

$$\frac{[Products]}{[Reactants]} > K_c$$

In this case, the reverse reaction will occur in order to attain equilibrium.

(ii) If ratio is less than K_c

$$\frac{[Products]}{[Reactants]} < K_c$$

This implies that more of the product is required to attain the equilibrium, therefore, the reaction will proceed in forward direction.

(iii) If ratio is equal to K_c

$$K_c = \frac{[Products]}{[Reactants]}$$

Then the reaction is at equilibrium.

Q. Why O_3 is unstable than O_2?

2. Extent of Reaction

(a) Very large K_c value

If the equilibrium constant (K_c) is very large, this indicates that the reaction is almost complete.

Example: Equilibrium constant for the decomposition of ozone to oxygen is 10^{55} at 25°C.

$$2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_c = 10^{55} \text{ at } 25°C$$

It infers that at room temperature, O_3 is unstable and decomposes very rapidly to O_2. This reaction is almost complete.

(b) Very small K_c value

If the value of K_c is very small, it reflects that the reaction does not proceed appreciably in the forward direction.

Example: The value of equilibrium constant for the decomposition of HF at 2000°C is 10^{-13}.

$$2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)} \qquad K_c = 10^{-13} \text{ at } 2000$$

It indicates high stability and slow decomposition of HF, even at 2000°C.

(c) K_c value neither large nor small

If the value of K_c is neither very large nor very small, it shows that both reactants and products are equally strong.

Example: $CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$ $K_c = 4$

3. The effect of conditions on the position of equilibrium

Equilibrium constant and position of equilibrium are two different entities.

- K_c is equilibrium constant and has constant value at a particular temperature.
- The ratio of products to reactants in equilibrium mixture is called equilibrium state. It can change if the external conditions like temperature, pressure and concentrations are changed.
- If K_c is large, then position of equilibrium lies on the right and if it is small then the position of equilibrium lies on left for a reversible reaction.

- K_c is an equilibrium constant expressed in terms of the concentrations of reactants and products.
- K_c is a constant for a particular reaction at a particular temperature.
- K_c is unaffected by changes in concentration or pressure and by the addition of the catalyst but varies with temperature.
- K_c can be calculated from the equilibrium concentrations of the reactants and products.

THE LE-CHATELIER'S PRINCIPLE

Statement

"If a stress is applied on a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the effect of that stress."

The system cannot completely cancel the effect of change, but will minimize it. The Le-Chatelier's principle has wide range of applications for ascertaining the position and composition of the physical and chemical equilibria.

(a) Effect of Change in Concentration

In order to understand the effect of change in concentration on the reversible reaction, consider the reaction in which $BiCl_3$ reacts with water to give a white insoluble compound BiOCl (artificial milk).

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

The equilibrium constant expression for the above reaction can be written as

$$K_c = \frac{[BiOCl][HCl]^2}{[BiCl_3][H_2O]}$$

Aqueous solution of $BiCl_3$ is cloudy because of hydrolysis and formation of BiOCl. If a small amount of HCl is added to the solution, it will disturb the equilibrium and force the system to move in such a way that effect of addition of HCl is minimized. The reaction will move in the backward direction to restore the equilibrium again and a clear solution will be obtained. However, if water is added to this solution, the system will move in the forward direction and the solution will again become cloudy. The shifting of reaction to forward and backward direction by disturbing the concentration is just according to Le-Chatelier's principle.

Conclusion

Addition of a substance among the reactants or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction. Similarly the addition of a substance among the products or the removal of a substance among the reactants will derived the equilibrium towards the backward direction. Removing one of the products formed can therefore increase the yield of a reversible reaction. The value of K_c however remains constant.

(b) Effect of Change in Volume or Pressure

The change in pressure and volume are important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal.

Example

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

This gas phase reaction proceeds with the decrease in number of moles and hence decreases in volume at equilibrium stage. When the reaction approaches the equilibrium stage, the volume of the equilibrium mixture is less than the volume of reactants taken initially. If one decreases the volume further at equilibrium stage, the reaction is disturbed. It will move to the forward direction to minimize the effect of disturbance. It establishes a new equilibrium position while K_c remains constant. The reverse happens when the volume is increased or pressure is decreased at equilibrium stage.

Note

If the pressure is increased in a reaction having unequal number of moles of reactants and products then the reaction will move in that direction where the number of moles are less.

(c) Quantitative Effect of Volume on Equilibrium Position

(i) Synthesis of SO_3

The quantitative effect of change of volume or pressure can be inferred from the mathematical expression of K_c for $SO_{3(g)}$ synthesis.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$K_c = \frac{4x^2V}{(a-2x)^2(b-x)}$$

Where,

- 'V' is the volume of reaction mixture at equilibrium stage.
- 'a' and 'b' are the number of moles of SO_2 and O_2 present initially.
- 'x' are the number of moles of oxygen reacted at equilibrium.

According to the above equation, when volume is increased, then 'x' has to be decreased to keep K_c constant. The decrease of 'x' means that the reaction is pushed towards backward direction. From the amount of the increase in volume, we can calculate the amount of 'x' which has to be decreased to keep K_c constant.

Similarly, by decreasing the volume (increasing the pressure), the value of K_c will increase. In order to keep the value of K_c constant, the reaction will move in the forward direction.

(ii) Dissociation of PCl_5

In the same way, effect of change of pressure on the equilibrium position can be explained for the dissociation of PCl_5. This is homogeneous gaseous phase reaction.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_2$$

K_c for this reaction is,

$$K_c = \frac{x^2}{(a-x)V}$$

(iii) Dissociation of N_2O_4

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

K_c for this reaction is,

$$K_c = \frac{4x^2}{(a-x)V}$$

Conclusion

In the dissociation of PCl_5 and N_2O_4, the factor of volume is present in the denominator. The reason is that number of moles of products are greater than those of reactants. So, increase in pressure will decrease the 'x' to keep the value of K_c constant and the reaction will be pushed to the backward direction. The equilibrium position is disturbed but not the K_c value.

Exceptional Behavior

- Those gaseous reactions in which number of moles of reactants and products are same, are not affected by change in pressure or volume.
- The reactions in which the participating substances are either liquids or solids, are not affected by change in pressure or volume.

(d) Effect of Change in Temperature

Most of the reversible chemical reactions are disturbed by change in temperature. If we consider heat as a component of equilibrium system, a rise in temperature adds heat to the system and a drop in temperature removes heat from the system. **According to Le-Chatelier's principle, a temperature increase favours the endothermic reactions and temperature decrease favours the exothermic reaction.**

For exothermic reactions

The equilibrium constant changes by the change of temperature, because the equilibrium position shifts without any substance being removed or added.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \qquad \Delta H = -41.84 \text{ kJ mol}^{-1}$$

- At equilibrium stage, if we take out heat and keep the system at this new lower temperature, the system will readjust itself, so as to compensate the loss of heat energy. Thus more CO and H_2O molecules will react to form CO_2 and H_2 molecules, thereby, liberating heat because reaction is exothermic in the forward direction. It means by decreasing temperature, we shift the initial equilibrium position to the right until a new equilibrium position is established.
- On the contrary, heating the reaction at equilibrium will shift the reaction to the backward direction because the backward reaction is endothermic.

For endothermic reactions

$$KI_{(s)} \rightleftharpoons KI_{(aq)} \qquad \Delta H = 21.4 \text{ kJ mol}^{-1}$$

Let us have a saturated solution of KI in water at given temperature. It has attained the equilibrium position. Now a rise in temperature at equilibrium favours the reaction to shift to the forward direction. On the other hand, decrease in temperature favours the reaction to shift towards the backward direction.

Effect of temperature on Solubility

Le-Chatelier's principle helps us to understand the effect of temperature on the solubility of different substances.

- Those substances, whose heats of solutions are negative, decrease their solubility by increasing temperature. e.g. LiCl, Li_2CO_3 etc.
- Those substances, whose heats of solutions are positive, increase their solubility by increasing temperature. e.g. KI, $Na_2B_4O_7$ (Borax), KNO_3 etc.
- For some salts, the heats of solution is close to zero (heat is neither evolved nor absorbed). The solubility of these salts in water is not affected by the change in temperature. e.g. Formation of aqueous solution of NaCl is an example of such a salt.

(e) Effect of Catalyst on Equilibrium Constant

In most of the reversible reactions, the equilibrium is not always reached within a suitable short time. So an appropriate catalyst is used.

- A catalyst does not affect the equilibrium position of the reactions. It increases the rates of both forward and backward reactions and this reduces the time to attain the equilibrium state.
- A catalyst lowers the energy of activation of both forward and reverse steps by giving new path to the reaction.

Change	Type or part of system	Effect on equilibrium
Pressure increasing	If there are more moles of gaseous products than gaseous reactants.	Shift to left
	If there are more moles of gaseous reactants than gaseous products.	Shift to right
Temperature increasing	If $\Delta H^\circ_{\text{forward reaction}}$ is positive, i.e. the forward reaction is endothermic.	Shift to right
	If $\Delta H^\circ_{\text{forward reaction}}$ is negative, i.e. the forward reaction is exothermic.	Shift to left
Concentration increasing	of reactants	Shift to right
	of products	Shift to left
Catalyst added		No effect

Q10. Explain the following with reasons:

(a) The change in volume disturbs the equilibrium positions for some reactions in gaseous phase but not the equilibrium constant.

Ans. (i) If reaction mixture is in gaseous state then at equilibrium if volume is changed it will effect the equilibrium

(ii) If number of moles of reactants are not equal to number of moles of product then those gaseous reactions are effected by volume change at equilibrium

For Example:

(i) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

(ii) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(b) The change of temperature disturbs both equilibrium position and constant of reaction.

Ans. The change of temperature disturbs both value of K_c and its equilibrium position because change in temperature changes heat contents of reaction mixture without changing concentration of reactants and products so with a change in position of equilibrium with temperature value of K_c is also changed.

(c) The solubility of glucose in water is increased by increasing temperature.

Ans. The solubility of glucose in water is endothermic process. It requires heat to be dissolved.

$$C_6H_{12}O_{6(s)} \rightleftharpoons C_6H_{12}O_{6(aq)} \qquad \Delta H = +ve$$

According to Le-chatelier's principle, an increase in temperature favours endothermic reaction. When temperature of the glucose solution is increased, the reaction moves in the forward direction. Hence, the solubility of glucose increases with the rise of temperature.

Q14. In the equilibrium.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = 90\,kJ\,mol^{-1}$$

What is the effect on?

(a) the position of equilibrium **(b) equilibrium constant? If**

(i) temperature increased **(ii) volume of the container is decreased**

(iii) catalyst is added **(iv) chlorine is added**

Explain your answer.

Ans. Equilibrium of:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = 90\,kJ\,mol^{-1}$$

(a) Position of equilibrium (b) Equilibrium constant

If

(i) **Temperature is increased:** Temperature change will affect both equilibrium position and equilibrium constant.

This is endothermic reaction, the increase of temperature shifts equilibrium positon in forward direction to re-establish equilibrium. Hence, the value of K_c increase.

(ii) **Volume is decreased:** The volume change affects equilibrium position only. When volume is decreased, reaction moves in backward direction to establish equilibrium again.

Since equilibrium constant has a constant value at a particular temperature, it is not affected by change in volume.

(iii) **Catalyst is added:** Catalyst has no effect on the equilibrium position and equilibrium constant. When catalyst is added at equilibrium, it enhances both the rates equally. Hence, equilibrium is not affected.

(iv) **Chlorine is added:** The addition of a substance at equilibrium affects the equilibrium position only. Equilibrium constant remains the same

When Cl_2 is added at equilibrium, the conc. of products increases and equilibrium position is shifted in backward direction

Applications of Chemical Equilibrium in Industry

Synthesis of ammonia by Haber's process

The proces of ammonia synthesis was developed by German Chemist F. Haber and first used in 1933.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92.46\ kJ$$

This process provides an excellent setting in which to apply equilibrium principle and see the compromises needed to make an industrial process economically worthwhile.

Ways to maximize yield of ammonia

Using Le-Chatelier's principle, one can have three ways to maximize the yield of ammonia.

(i) By continual withdrawal of ammonia after intervals, the equilibrium will shift to forward direction in accordance with Le-Chatelier's principle

(ii) Increase the pressure to decrease the volume of the reaction vessel. Four moles of the reactants combine to give two moles of products. High pressure will shift the equilibrium position to right to give more and more ammonia.

(iii) Decreasing the temperature will shift it to the forward direction according to Le-Chatelier's principle.

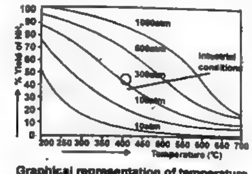
So high pressure, low temperature and continual removal of ammonia will give the maximum yield of ammonia.

Effect of Temperature on K_c

The table shows that for the regular increase in temperature the value of K_c decreases irregularly.

T(K)	K_c
200	7.17×10^{15}
300	2.69×10^{8}
400	3.94×10^{4}
500	1.72×10^{2}
600	4.53×10^{0}
700	2.96×10^{-1}
800	3.96×10^{-2}

Graphical representation of temperature and pressure for NH_3 synthesis



Graphical representation of temperature and pressure for NH_3 synthesis

A graph is plotted between percentage yield of ammonia vs. temperature at five operating pressures. At very high pressure and low temperature, the yield of NH_3 is high but the rate of reaction is very low. Industrial conditions denoted by circle are between 200 and 300 atmospheres at about 400°C.

Explanation

No doubt the yield of NH_3 is favoured at low temperature but the rate of its formation does not remain favourable. The rate becomes so slow and the process is rendered uneconomical. To optimize the yield and the rate the temperature is raised to a moderate level and a catalyst is employed to increase the rate. If one wants to achieve the same rate without a catalyst, then it requires much higher temperature, which lowers the yield.

Optimum conditions

The optimum conditions for the above reaction are:

- **Temperature:** 400°C (673 K)
- **Pressure:** 200-300 atm
- **Catalyst:** pieces of iron crystals embedded in a fused mixture of MgO, Al_2O_3 and SiO_2.

Distillation of ammonia

The equilibrium mixture has 35% by volume of ammonia. The mixture is cooled by refrigeration coils until ammonia condenses (B.P = −33.4°C) and is removed. Since, boiling points of nitrogen and hydrogen are very low, they remain in the gaseous state and are recycled by pumps back into the reaction chamber

Economic importance

Nearly 13% of all nitrogen fixation on earth is accomplished industrially through Haber's process. This process synthesizes approximately 110 million tons of ammonia in the world. About 80% of this is used for the production of fertilizers and some is used in manufacture of explosives or the production of nylon and other polymers.

Q15. Synthesis of ammonia by Haber's process is an exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92.46\ kJ\,mol^{-1}$$

(a) What should be the possible effect of change of temperature at equilibrium state?

(b) How does the change of pressure or volume shifts the equilibrium position of this reaction?

(c) What is the role of catalyst in this reaction?

(d) What happens to equilibrium position of this reaction if NH_3 is removed from the reactionvessel from time to time?

Ans.

(a) Since reaction is endothermic in backward direction, rise of temperature will shift equilibrium to left. Low temperature shfits the equilibrium to right and yield of NH_3 will increase

(b) Increase of pressure decreases the volume and equilibrium position is shifted in forward direction. As a result yield of ammonia increases and vice versa.

(c) Catalyst have no effect on the position of equilibrium. However, it helps the equilibrium to establish earlier. And we obtain the maximum yield of ammonia at faster rate.

(d) Continuous removal of NH_3 from reaction vessel from time to time, shifts reaction in forward direction, and we get maximum yield of NH_3.

Preparation of Sulphur Trioxide (SO_3)

Contact process is used for the manufacturing of H_2SO_4 on industrial scale in which the conversion of SO_2 to SO_3 is achieved in a reversible reaction.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -194\ kJ\ mol^{-1}$$

Ways to maximize yield of SO_3

- At low temperature, the equilibrium constant for formation of SO_3 is large but equilibrium is reached very slowly. As the temperature is raised the rate increases but the yield of SO_3 drops off according to Le-Chatelier's principle.
- High pressure tends to increase yield of SO_3. However, instead of using high pressure; the concentration of O_2 (air) is increased to increase the yield of SO_3.

Effect of temperature on the yield of SO_3

The table helps to understand the effect of different conditions on the yield of SO_3. During the process pressure is kept at one atmosphere

Temperature (°C)	K_c	Mole% of SO_3
200	5500	98
300	690	91
400	160	75
500	55	61
600	25	46
700	13	31

Optimum conditions

To have the best possible yield of SO_3 within a reasonable time, a mixture of SO_2 and O_2 (air) at 1 atm pressure is passed over a solid catalyst at 650°C. The equilibrium mixture is then recycled at lower temperature, 400-500°C, to increase the yield of SO_3. The most effective catalyst are V_2O_5 and finely divided platinum. SO_3 is dissolved in H_2SO_4 to get oleum, which is diluted to get H_2SO_4.

Economic importance

H_2SO_4 is the king of chemicals. A country's industrial progress is measured by the amount of H_2SO_4 manufactured each year

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Q16. (a) Sulphuric acid is the king of chemicals. It is produced by the burning of SO_2 to SO_3 through an exothermic reversible process.

(a) Write the balanced reversible reaction.

(b) What is the effect of pressure change on this reaction?

(c) Reaction is exothermic but still the temperature of 400–500°C is required to increase the yield of SO_3. Give reasons.

Ans.

(a) $$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)} \qquad (\Delta H = -194\ kJmol^{-1})$$

(b) Increase of pressure shifts the reaction in forward direction (less number of moles are produced) and vice versa

(c) For this exothermic reaction, if the temperature is kept low, the reaction will be slow but yield of SO_3 will be high. Due to slow rate of reaction, it becomes uneconomical. To make the process economical temperature is maintained at 400–500°C so that SO_3 is obtained at faster rate. In this we get maximum yield of SO_3 in short time which is economical.

IONIC PRODUCT OF WATER

Pure water is very poor conductor of electricity but its conductance is measurable. Water undergoes self ionization as follows and the reaction is reversible.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The equilibrium constant for this reaction is given as:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} = 1.8 \times 10^{-16}\ mol\ dm^{-3}$$

The concentrations of H_2O i.e. $[H_2O]$ in pure water may be calculated to be 1000 g dm^{-3} divided by 18 g mol^{-1} giving 55.5 moles dm^{-3}.

Since water is present in very large excess and very few of its molecules undergo ionization, so its concentration remains effectively constant. Constant concentration of water is taken on L.H.S and multiplied with K_c to get another constant called K_W.

$$K_c[H_2O] = [H^+][OH]^- \text{ ------------ (i)}$$

$$1.8 \times 10^{-16} \times 55.5 = 1.01 \times 10^{-14} = [H^+][OH^-]$$

This 1.01×10^{-14} is called K_w of water at 25°C.

$$K_w = [H^+][OH]^- = 10^{-14} \text{ at } 25°C$$

K_w is called ionic product of water or dissociation constant of water. The value of K_w increases almost 75 times when the temperature is increased from 0°C to 100°C. Anyhow the increase in K_w is not regular.

TEMP. (°C)	K_w
0	0.11×10^{-14}
10	0.30×10^{-14}
25	1.0×10^{-14}
40	3.00×10^{-14}
100	7.5×10^{-14}

Whenever some quantity of acid or base is added in water, then K_w remains the same, but $[H^+]$ and $[OH^-]$ are no more equal.

In neutral water:

$$[H^+] = [OH^-]$$

$$[H^+][H^+] = 10^{-14}$$

$$[H^+]^2 = 10^{-14}$$

$$[H^+] = 10^{-7} \text{ moles } dm^{-3}$$

Similarly $$[OH^-] = 10^{-7}\ mol\ dm^{-3}$$

This means that out of 55.5 moles of pure water in one dm^3 of it, only 10^{-7} moles of it are dissociated into ions. This shows that water is a very weak electrolyte.

At 40°C, the $[H^+] = [OH^-]$ but the values are less than 10^{-7} moles dm^{-3} and pure water is again neutral at 40°C. Similarly, pure water is neutral at 100°C, $[H^+]$ and $[OH]$ are greater than those at 40°C.

In the case, addition of small amount of an acid.

$$[H^+] > [OH^-]$$

In the case of addition of few drops of a base.

$$[OH^-] > [H^+]$$

During both of these additions, the value of K_w will remain the same i.e., 10^{-14} at 25°C.

Sorenson's contribution

Actually, in all the aqueous solutions, the concentration of H^+ and OH^- are too low to be conveniently expressed and used in calculations. In 1909, Sorenson, a Danish biochemist, introduced the term pH and pOH. So, the scales of pH and pOH have been developed.

pH:

"The negative log of hydrogen ion concentration is called pH."

$$pH = -\log[H^+]$$

pOH:

"The negative log of concentration of hydroxide ion is called pOH."

$$pOH = -\log[OH^-]$$

Relationship between pH and pOH with pK_w

$$pK_w = pH + pOH = 14$$

The sum of pH and pOH for a solution must be equal to 14.

For neutral solution pH = 7

For acidic solution pH less than 7

For basic solution pH more than 7

pK_w:

"The negative logarithm of K_w is called pK_w."

$$K_w = [H]^{+}[OH]^{-} = 10^{-14}$$

$$-\log K_w = -\log[H^+][OH]^- = -\log 10^{-14}$$

$$pK_w = -\log[H^+] + (-\log[OH^-]) = 14 \log 10$$

$$pK_w = pH + pOH = 14 \text{ (at } 25°C)$$

A hydrogen ion, H^+ is simply a hydrogen atom with an electron removed. Because a hydrogen atom comprises one proton and one electron, removing the electron leaves just a proton. 'H^+' Hydrogen ion' and proton refer to the same thing.

- The value of pK_w is less than 14 at higher temperatures i.e. at 40°C and 100°C.
- The value of pH normally varies between $0 \rightarrow 14$ at 25°C.
- There are some solutions whose pH is being determined in negative while some solutions have pH more than 14.
- For a solution, having concentration of H^+ ion more than 1M, its pH will be in negative.
- For the solution, having $[OH^-]$ more than 1M, its pH will more than 14.

Relationship of $[H_3O^+]$, $[OH^-]$, pH and pOH

	$[H_3O^+]$	pH	$[OH^-]$	pOH
Basic	1×10^{-14}	14.0	1×10	0.0
	1×10^{-13}	13.0	1×10^{-1}	1.0
	1×10^{-12}	12.0	1×10^{-2}	2.0
	1×10^{-11}	11.0	1×10^{-3}	3.0
	1×10^{-10}	10.0	1×10^{-4}	4.0
	1×10^{-9}	9.0	1×10^{-5}	5.0
	1×10^{-8}	8.0	1×10^{-6}	6.0
Neutral	1×10^{-7}	7.0	1×10^{-7}	7.0
Acidic	1×10^{-6}	6.0	1×10^{-8}	8.0
	1×10^{-5}	5.0	1×10^{-9}	9.0
	1×10^{-4}	4.0	1×10^{-10}	10.0
	1×10^{-3}	3.0	1×10^{-11}	11.0
	1×10^{-2}	2.0	1×10^{-12}	12.0
	1×10^{-1}	1.0	1×10^{-13}	13.0
	1×10^{0}	0.0	1×10^{-14}	14.0

Approximate pH and pOH of some common materials at 25°C

Material	pH	pOH	Material	pH	pOH
1.0 M HCl	0.1	13.9	bread	5.5	8.5
0.1 M HCl	1.1	12.9	potatoes	5.8	8.2
0.1 M CH_3COOH	2.9	11.10	rainwater	6.2	7.8

gastric juice	2.0	12.00	milk	6.5	7.5
lemons	2.3	11.7	saliva	6.5-6.9	7.5-7.1
vinegar	2.8	11.2	pure water	7.0	7.00
soft drinks	3.0	11.00	eggs	7.8	6.2
apples	3.1	10.9	0.1 M $NaHCO_3$	8.4	5.6
grapefruit	3.1	10.9	sea water	8.5	5.5
oranges	3.5	10.5	milk of magnesia	10.5	3.5
tomatoes	4.2	9.8	0.1 M NH_3	11.1	2.9
cherries	3.6	10.4	0.05 M Na_2CO_3	11.6	2.4
bananas	4.6	9.4	0.1 M NaOH	13.0	1.00

Q11. (a) What is an ionic product of water? How does this value vary with the change in temperature? Is it true that its value increase 75 times when the temperature of water is increased form 0°C to 100°C.

(b) What is the justification for the increase of ionic product with temperature?

(c) How would you prove that at 25°C 1 dm^3 of water contains 10^{-7} moles of H_3O^+ and 10^{-7} moles of OH^-.

Ans. (a) Ionic Product of water: The product of molar concentration of H^+ and OH^- in pure water is called ionic product of water. It is represented by K_w and its value is 10^{-14} at 25°C.

$$K_w = [H^+][OH^-]$$

$$K_w = 10^{-14}$$

K_w and Change of Temperature: The value of K_w is directly proportional to the temperature. Higher the temperature, greater will be the value of K_w, because at high temperature ionization of water increases and ionic concentration of water is also increased e.g.

$$K_w = 0.1\times10^{-14} \text{ at } 0°C$$

and

$$K_w = 1\times10^{-14} \text{ at } 25°C$$

K_w at 0°C and 100°C: Yes, it is true that value of K_w increases 75 times when temperature of water is raised from 0°C to 100°C. The value of $K_w = 0.1\times10^{-14}$ at 0°C and $K_w = 7.5\times10^{-14}$.

This can be shown as (Ionic product of water at 0°C x 75) Ionic product of water at 100°C

$$0.1\times10^{-14}\times75 = 7.5\times10^{-14}$$

This comparison verifies that ionic product of water at 100°C is 75 times of the value of 0°C.

(b) When temperature increases, then ~~ionic concentration of water increases with the~~ increasing ionic concentration, ionic product of water (K_w) also increases.

(c) Ionic product of water is:

$$K_w = [H^+][OH^-]$$

$$10^{-14} = [H^+][OH^-] \quad \text{.................(I)}$$

Water ionizes as $H_2O \rightleftharpoons H^+ + OH^-$.

It shows that in case of pure water:

$$[H^+] = [OH]^-$$

Hence, we can write eq. (I) as:

$$10^{-14} = [H^+][H^+] \quad \text{since, } [H^+] = [OH]^-$$

$$10^{-14} = [H^+]^2$$

Taking square root on both sides:

$$10^{-7} = [H^+] \text{ moles/dm}^3 \quad \text{since, } [H^+] = [H_3O^+]$$

Hence, $$10^{-7} = [OH^-] \text{ moles/dm}^3$$

Q12. (a) Define pH and pOH. How are they related with pK_w.
(b) What happenes to the acidic and basic properties of aqueous solutions when pH varies from zero to 14?
(c) It is true that sum of pK_a and pK_b is always equal to 14 at all temperature for any acid? If not, why?

Ans. (a) pH: "The negative logarithm of hydrogen ion concentration in the solution is called pH."

$$pH = -\log[H^+]$$

pOH: "the negative logarithm of hydroxide ion concentration in the solution is called pOH

$$pOH = -\log[OH^-]$$

Relation of pH and pOH with pK_w: From the concept of ionic product of water we have

$$K_w = [H^+][OH^-]$$

Taking log:

$$\log K_w = \log[H^+] + \log[OH^-]$$

Now multiply with (-1)

$$-\log K_w = -\log[H^+] + (-\log[\overline{O}H])$$

$$pK_w = pH + pOH$$

$$pH + pOH = 14 \text{ at } 25°C \qquad (\text{Since, } pK_w = 14 \text{ at } 25°C)$$

Equation (i) shows that the sum of pH and pOH is equal to pK_w i.e. 14 at 25°C.

(b) When pH value varies from zero to 7, acidic properties of aqueous solution increases.
The solution is acidic when pH value is between zero and 7 and is basic when pH value is between 7 and 14

(c) No, it is not true always. Lets understand it at two different temperatues.

(i) Sum of pK_a and pK_b at 25°C.

$$pK_a + pK_b = pK_w \quad pK_w = -\log K_w$$

$$K_w = 10^{-14} \text{ at } 25°C.$$

$$pK_a + pK_b = -\log K_w$$

$$pK_a + pK_b = -\log 10^{-14}$$

$$pK_a + pK_b = 14 \qquad \log^1_{10} = 1$$

It is true at 25°C.

(ii) Sum of pK_a and pK_b at 100°C.

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = -\log K_w$$

$$pK_a + pK_b = -\log(7.5 \times 10^{-14}) \quad K_w = 7.5 \times 10^{-14} \text{ at } 100°C$$

$$pK_a + pK_b = 13.125$$

Hence at 100°C, the sum of pK_a and pK_b is less than 14.

The reason for this is that the value of ionization constant (K_w) of water has greater value and its $-\log(pK_w)$ has lesser value than that at 25°C.

...ation constants of acids (K_a)

The ionization constants of the acids is the quantitative measure of the strength of the acid. Acids and bases when dissolved in water may or may not be completely dissociated. Many acids are weak electrolytes and they ionize to an extent which is less than 100 %.

Derivation of K_a

Suppose we have a monoprotic acid (HA) which ionizes in water as follows:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

K_c for this reversible reaction can be written as

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

At the equilibrium stage, the concentration of H_2O is almost the same as at the initial stages because it has been taken in large excess. A reasonable approximation, therefore, is to take the concentration of water to be effectively constant and take it on the left hand side with K_c.

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_c[H_2O] = K_a$$

Hence, $$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Applications

This equation can be used to calculate.

(i) K_a for any acidic solution if we know the pH or Hydrogen ion concentration $[H^+]$ of that solution and the initial concentration of acid [HA] dissolved.

(ii) The equilibrium concentration of $[H_3O^+]$ and $[A^-]$ produced if we know the initial concentration of acid [HA] and its K_a value.

Important points

(i) If K_a is less than 10^{-3}

Then the acid will be weak

CH_3COOH	$K_a = 1.85 \times 10^{-5}$	Weak acid
H_2S	$K_a = 1.0 \times 10^{-7}$	Weak acid
H_2O	$K_a = 1.85 \times 10^{-16}$	Very weak acid

(ii) If $K_a = 1$ to 10^{-3}

Then the acid will be moderately strong.

(iii) If $K_a > 1$

Then the acid will be strong.

Example

HCl	$K_a = 10^7$	Very strong acid
HNO_3	$K_a = 10^3$	Very strong acid
H_2SO_4	$K_a = 10^2$	Very strong acid

Dissociation constants of some acids at 25°C and their relative strength

Acid	Dissociation	K_a	Relative strength
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	very large (10^{+7})	very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^{-1}$	very large (10^{+3})	very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	large (10^{+2})	very strong

HSO_4	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.3×10^{-4}	strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-5}	weak
CH_3COOH	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.85×10^{-5}	weak
H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^{-1}$	4.4×10^{-7}	weak
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	weak
NH_4^+	$NH_4 \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	weak
HCO_3^-	$HCO_3 \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-11}	weak
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-16}	very weak

Percentage of Ionization of Acids

We can calculate the percentage of weak acid and the formula is as follows:

$$\%\text{ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}}\times100$$

Ostwald's Dilution law

The degree of dissociation of a weak electrolyte is proportional to the square root of dilution.

Factor

The percentage ionizations of weak acids depend upon the extent of dilution of their aqueous solutions.

Explanation

Table shows the change in percentage ionization of acetic acid at different concentrations. Lesser the molarity, diluted the solution, greater the chances for electrolyte to be dissociated.

- When 0.1 moles of CH_3COOH is dissolved in $1000cm^3$ of solution, then 1.33 molecules are dissociated out of 100, and 13.3 out of 1000.
- When the 0.001 moles are dissolved per dm^3 of solution then 12.6 molecules of CH_3COOH get dissociated out of 1000. Remember that K_a remains the same at all dilutions at a constant temperature.

Percentage ionization and ionization constants of acetic acid at 25°C

Molarity	% ionized	$[H_3O^+]$	$[CH_3COOH]$	K_a
0.10000	1.33	0.001330	0.098670	1.79×10^{-5}
0.0500	1.89	0.000945	0.049060	1.82×10^{-5}
0.0100	4.17	0.000417	0.009583	1.81×10^{-5}
0.0050	5.86	0.000293	0.004707	1.81×10^{-5}
0.0010	12.60	0.000126	0.000874	1.72×10^{-5}

pK_a:

The negative log of dissociation constant of acid (K_a) is called pK_a:

$$pK_a = -\log K_a$$

Reasoning of pK_a instead of K_a

The values of K_a for weak acids are very small numbers usually expressed in exponential form. So it is convenient to convert them into whole number by taking their negative logarithm.

Relationship between K_a and pK_a

$$\left(pK_a \propto \frac{1}{K_a}\right)$$

Larger the value of pK_a, weaker will be the acid and vice versa.

The pk_a scale

Since k_a value are very small it is convenient to use the pk_a scale where

$pk_a = -\log_{10}k_a$

For example

$k_a = 1.70\times10^{-5}\ moldm^{-3}$

Then $pk_a = -\log_{10}(1.70\times10^{-5})$

$= 4.77$

If $k_a = 2.30\times10^{-7}\ moldm^{-3}$ then

$pk_a = 6.63$.

Important points

If the difference of pK_a value of two acids is '1' then acid with smaller pKa is 10 times stronger than the other. If the difference is 2 then one is hundred times stronger than the other.

Ionization constants of bases (K_b)

"The ionization constants of bases (K_b) are quantitative measure of strength of the bases."

Unlike, strong bases weak Bronsted bases which are proton acceptors, usually consist of molecules or ions. They react with water, remove a proton from it, and generate OH^- ions. Take the examples of NH_3 and CO_3^{2-}.

$$CO_3^{-2}{}_{(aq)} + H_2O_{(\ell)} \rightleftharpoons HCO_3^{-1}{}_{(aq)} + OH^-_{(aq)}$$

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

NH_3 and CO_3^{2-} have acted as bases in above reactions. They have different abilities to accept protons from water molecules. We compare these abilities of bases by knowing the equilibrium constant K_b, which is called base ionization constant of a base.

Derivation of K_b

Consider a general reaction:

$$B_{(aq)} + H_2O_{(\ell)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

Since, the concentrations of H_2O is constant, being in large excess.

$$K_c[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

$$K_c[H_2O] = K_b$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

So K_b value of a base is the quantitative measurement of strength of base. Smaller the K_b value, weaker the base and vice versa.

K_b of some important bases

Base	Dissociation	K_b	Relative strength
NaOH	$NaOH \rightleftharpoons Na^+ + OH^+$	Very high	Very strong
KOH	$KOH \rightleftharpoons K^- + OH$	Very high	Very strong
$Ca(OH)_2$	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	High	Strong
NH_4OH	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.81×10^{-5}	Weak
CH_3NH_2 (Methylamine)	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.38×10^{-4}	Weak
$C_6H_5NH_2$ (Aniline)	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.7×10^{-10}	Very weak

pK_b:

"The negative log of K_b is called pK_b."

$$pK_b = -\log K_b$$

Reasoning of pK_b instead of K_b

The values of K_b for weak bases are very small numbers. Usually expressed in exponential form. It is convenient to convert them into whole numbers by taking their negative log.

Relationship between K_b and pK_b

$$pK_b \propto \frac{1}{K_b}$$

Larger the value of pK_b, weaker will be the base and vice versa.

Important points

- If the difference of pK_b values of two bases is '1' then base with smaller pK_b is ten times stronger than the other.
- If the difference of pK_b values of two bases is '2' then base with smaller pK_b is 100 times stronger than the other.

Q13. (a) What is Lowry Bronsted idea of acids and bases: Explain conjugate acid and bases.

Lowry Bronsted Acid and Base Concept

Introduction

J.M Lowry and J.W Bronsted gave this concept independently in 1923. According to this concept:

Acid

"Those species (ions or molecules) which donate or have a tendency to donate proton (H^+) are called acids."

Example

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \xrightarrow{H^+} H_3O^+ + Cl^-$$

Base

"These species (ions or molecules) which accept or have a tendency to accept proton $(H^+)$are called bases."

Example

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_2O} \xrightarrow{H^+} NH_4^+ + OH^-$$

- A Bronsted-Lowery acid is a proton donor.
- A Bronsted-Lowery base is a proton acceptor.
- The strength of an acid or base is determined by the degree of dissociation; Strong acids/bases are fully dissociated in solution whilst weak acids/bases are only partially dissociated in solution.

Conjugate acid-base pair

When a weak acid or a weak base is dissolved in water, the conjugate acid base pair is produced.

e.g., $$\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{CH_3COO^-} + \underset{\text{conjugate acid}}{H_3O^+}$$

Note

Some compounds behave both as acids as well as base therefore called as amphoteric compounds e.g., water, HSO_4^-, HCO_3^{-1}

MCQ

Which of the following is strongest base?

(a) F^- (b) Cl^-
(c) Br^- (d) I^-

Relationship between K_a, K_b and K_w

There is a close relationship between K_a and K_b of the conjugate base and K_w of water.

Let us we have an acid HA and it gives proton to water in a reversible manner. H_3O^+ gives proton to A^- and is an acid but A^- accepts H^+ from H_3O^+ and acts as conjugate base of HA.

$$\underset{\text{Acid}}{HA} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate Acid}}{H_3O^+} + \underset{\text{Conjugate Base}}{A^-}$$

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_c[H_2O] = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad ......(i)$$

In the case, A^- when dissolved in water, the equation for hydrolysis of conjugate base A^- will be

$$\underset{\text{base}}{A^-} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{HA} + \underset{\text{base}}{OH^-}$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad ......(ii)$$

Let us multiply two expressions for K_a and K_b.

$$K_a \times K_b = \frac{[H^+][A^-]}{[HA]} \times \frac{[OH^-][HA]}{[A^-]}$$

$$K_a \times K_b = [H^+][OH^-]$$

$$K_a \times K_b = K_w, \quad K_w = 10^{-14} \text{ at } 25°C$$

This equation is useful if we know K_a of acid, we can calculate K_b of the conjugate base and vice versa. The value of K_w is a constant at a given temperature i.e. 14 at 25°C and less than 14 at higher temperatures

Let us take the log of above equation

$$\log(K_a \times K_b) = \log(K_w)$$

$$\log K_a + (\log K_b) = \log K_w$$

Multiply both sides by '-1'

$$-\log K_a - \log K_b = -\log K_w$$

Since $pK_a = -\log K_a$ and $pK_b = -\log K_b$

So $$pK_a + pK_b = pK_w = 14$$

Hence pK_a and pK_b of conjugate acid base pair has a very simple relation with each other.

$$pK_a + pK_b = 14 \text{ at } 25°C$$

This equation proves the following facts:

(a) Conjugate base of a very weak acid is relatively very strong base.
(b) Conjugate acid of a very strong base is relatively very weak acid.

So $K_a \propto 1/K_b$

We can calculate the pK_b of CH_3COO^- if we know pK_a of CH_3COOH and if we know pK_b of NH_3, we can calculate pK_a of NH_4^+

Q13. (b) Acetic acid dissolves in water and gives proton to water, but when dissolved in H_2SO_4, it accepts protons. Discuss the role of acetic acid in both cases.

Ans. (b) When acetic acid is dissolved in water, it undergo dissociation as:

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons CH_3COO^- + H_3O^+$$

Acetic acid donates a proton to water and acts as an acid whereas water accepts a proton from acetic acid and acts as base.

When acetic acid is dissolved in H_2SO_4, it undergoes dissociation as:

$$\underset{\text{Base}}{CH_3COOH} + \underset{\text{Acid}}{H_2SO_4} \rightleftharpoons CH_3COO^+H_2 + HSO_4^-$$

H_2SO_4 being more stronger acid donates a proton to acetic acid and acts as an acid whereas CH_3COOH being weak acid accepts a proton from sulphuric acid and behaves as a base.

conjugate pair

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{CH_3COOH} \rightleftharpoons \underset{\text{Acid conjugate}}{NH_4^+} + \underset{\text{Base conjugate}}{CH_3COO^-}$$

conjugate pair

COMMON ION EFFECT

"The suppression of ionization of a weak electrolyte by adding a common ion from outside is called common ion effect."

Example: Purification of NaCl

NaCl is purified by passing hydrogen chloride gas through the saturated brine. Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$K_c = \frac{[Na^+][Cl^-]}{[NaCl]}$$

HCl also ionizes in solution.

$$HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

On passing HCl gas, concentration of Cl^- ions is increased. Therefore, NaCl crystallizes out of the solution to maintain the constant value of equilibrium constant. This type of effect is called common ion effect.

The addition of a common ion to the solution of less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

$$Na^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons NaCl_{(s)}$$

More examples of common ion effect

1. The solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of more soluble salt KCl by common ion effect. K^+ is a common ion. The ionization of $KClO_3$ is suppressed and it settles down as precipitate.

$$KClO_{3(s)} \rightleftharpoons K^+_{(aq)} + ClO^{-1}_{3(aq)}$$

$$KCl \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

2. Similarly the dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion. H_2S becomes less dissociated in acidic solution. In this way, low concentration of S^{-2} is developed.

$$H_2S \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

This low concentration of S^{2-} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

3. An addition of NH_4Cl in NH_4OH solution suppresses the concentration of $OH^-_{(aq)}$ due to the presence of a large excess of NH_4^+ from NH_4Cl. Actually, NH_4Cl is a strong electrolyte. The combination of these two substances is used as reagent in third group basic radicals.

$$NH_4Cl_{(aq)} \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)}$$

$$NH_4OH_{(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

4. Common ion effect finds its extensive applications in the qualitative analysis and the preparation of buffers

Q7 (a) What are buffer solutions? Why do we need them in daily life?
(b) How does the mixture of sodium acetate and acetic acid give us the acidic buffer?
(c) Explain that a mixture of NH_4OH and NH_4Cl gives us the basic buffer.

BUFFER SOLUTIONS

"Those solutions which resist the change in their pH when a small amount of an acid or a base is added to them are called Buffer solution."

- The buffer solutions have a specific constant value of pH.
- The pH values of buffer solutions do not change on dilution and on keeping for a long time.

Although the two components in a buffer solution react with added acid and alkali, they cannot stop the pH from changing. They do however minimize pH changes.

Types of buffer solutions

Buffer solutions are mostly prepared by mixing two substances.

Acidic buffers	Basic buffers
• Those buffers which are formed by the mixing of a weak acid and a salt of it with a strong base are called acidic buffers.	• Those buffers which are formed by mixing of a weak base and a salt of it with a strong acid are called basic buffers.
• Their pH is usually less than 7.	• Their pH is more than 7
• Henderson's equation for acidic buffers $pH = pK_a + \log\frac{[salt]}{[acid]}$	• Henderson's equation for basic buffers $pOH = pK_b + \log\frac{[salt]}{[base]}$
e.g. $CH_3COOH + CH_3COONa$ (Acetic acid) (Sodium acetate) (Weak acid) (Salt of acetic acid)	e.g. NH_4OH + NH_4Cl (Weak base) (Salt of weak base) (Ammonium hydroxide) (Ammonium chloride)

Why Do We Need Buffer Solution

1. pH of human blood maintains at 7.35, if it goes to 7.00 or 8.00, a person may die. So human blood is a natural buffer which maintains its pH.
2. Sometimes one wants to study a reaction under conditions that would suffer any associated change in the pH of reaction mixture. So, by a suitable choice of the solutes, a chemist can ensure that a solution will not experience more than a very small change in pH, even if small amount of a strong acid or a strong base is added.
3. Buffers are important in many areas of chemistry and allied sciences like molecular biology, microbiology, cell biology, soil sciences, nutrition and the clinical analysis.

Q7. (d) How do you justify that the greater quantity of CH_3COONa in acetic acid decreases the dissociating power of acetic acid so the pH increases.

How Do the Buffers Act

Let us take the example of an acidic buffer consisting of CH_3COOH and CH_3COONa. Common ion effect will help to understand how the buffer will work. CH_3COOH, being a weak electrolyte undergoes very little dissociation. When CH_3COONa which is a strong electrolyte, is added to CH_3COOH solution, then dissociation of CH_3COOH is suppressed due to common ion effect of CH_3COO^-

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$CH_3COONa_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

If one goes on adding CH_3COONa in CH_3COOH solution, then the added concentrations of CH_3COO^- decrease the dissociation of CH_3COOH and the pH of the solution increases.

Greater the concentration of acetic acid as compared to CH_3COONa, lesser is the pH of solution.

$[CH_3COOH]$ (mol. dm^{-3})	$[CH_3COO^-]$ (mol dm^{-3})	% Dissociation	pH
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

Actually, this buffer is a large reservoir of CH_3COOH and CH_3COO^- components. When an acid or H_3O^+ are added to this buffer, they will react with CH_3COO^- to give back acetic acid and hence the pH of the solution will almost remain unchanged.

Reason

The reason is that CH_3COOH being a weak acid will prefer to remain undissociated. Similarly, the buffer solution consisting of NH_4Cl and NH_4OH can resist the change of pH and pOH, when acid or a base is added from outside. When a base or OH^- ions are added in it, they will react with H_3O^+ to give back H_2O and the pH of the solution again will remain almost unchanged.

Henderson's Equation for Acidic Buffers

Consider a weak acid HA and its salt NaA with a strong base NaOH. The reversible reactions for dissociation of HA and NaA are as follows:

$$HA \rightleftharpoons H^+ + A^-$$
$$NaA \rightleftharpoons Na^+ + A^-$$

The dissociation constant of a weak acid HA is given by:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Rearranging the equation:

$$[H^+] = \frac{K_a[HA]}{[A^-]}$$

The concentration of A^- in the reaction mixture is **predominantly being supplied by NaA** which is a stronger electrolyte than HA and the ionization of HA is being suppressed by common ion effect. (A^- is the common ion in this buffer solution).

Taking log of this equation:

$$\log[H^+] = \log\frac{K_a[HA]}{[A^-]}$$

$$\log[H^+] = \log K_a + \log\frac{[HA]}{[A^-]}$$

Multiplying with negative on both sides, we get

$$-\log[H^+] = -\log K_a + \left(-\log\frac{[HA]}{[A^-]}\right)$$

$$-\log[H^+] = pH$$
$$-\log K_a = pK_a$$

So

$$pH = pK_a - \log\frac{[HA]}{[A^-]}$$

$[A^-]$ refers to the concentration of the salt. Actually, maximum possible concentration of A^- is given by NaA being a strong electrolyte

$$pH = pK_a - \log\frac{[acid]}{[salt]}$$

Interchanging the numerator and denominator, the sign of log changes.

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

This relationship is called Henderson's equation. This equation shows that two factors evidently govern the pH of a buffer solution.

(i) pK_a of acid used.

(ii) Ratio of concentrations of the salt and the acid.

Formation of different buffer solutions

The best buffer solution is prepared by taking equal concentration of the acid and the salt. So, pH is controlled by pK_a

Example 1

$$[CH_3COOH] = [CH_3COONa]$$
$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$
$$pH = pK_a + \log(1)$$
$$pH = pK_a + 0$$
$$pH = 4.74$$

It means that if concentration of salt and acid are equal then pH is equal to pK_a.

Example 2

If concentration of formic acid and sodium format are equal then

$$[HCOOH] = [HCOONa]$$
$$pH = pK_a + 0 = pK_a$$
$$pH = 3.78$$

Example 3

To prepare a buffer of definite pH, we need a suitable acid for that purpose. We can also manage the buffer of our own required pH by suitably selecting the concentration ratio of the acid and the salt. If

$$[CH_3COOH] = 0.1\ moles.dm^{-3}$$
and
$$[CH_3COONa] = 1\ moles.dm^{-3}$$
$$pH = 4.74 + \log\frac{[salt]}{[acid]}$$
$$pH = 4.74 + \log\frac{1.0}{0.1} = 4.74 + \log 10$$
$$\log 10 = 1$$
$$pH = 4.74 + 1 = 5.74$$
$$pH = 5.74$$

Example 4

$$[CH_3COOH] = 1\ moles.dm^{-3}$$
$$[CH_3COONa] = 0.1\ moles.dm^{-3}$$

then,

$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$
$$= 4.74 + \log\frac{0.1}{1.0}$$
$$= 4.74 + \log 10^{-1}$$
$$= 4.74 + -\log 10$$
$$= 4.74 - 1$$
$$pH = 3.74$$

The above mentioned combination can be used to prepare buffers from pH 3.74 to 5.74. The buffer beyond this range will not be good buffers and will have small buffer capacities.

Henderson's Equation for Basic Buffer

Let us use the mixture of NH_4OH and NH_4Cl. NH_4OH is a solution of NH_3 in water and can be represented as follows:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Taking the log, multiplying with negative sign and rearranging, we get

$$pOH = pK_b + \log\frac{[salt]}{[base]}$$

Using this relationship, we can prepare a basic buffer of the required pOH or pH by suitably selecting a base and adjusting the ratio of $\frac{[salt]}{[base]}$

Note: For equal concentration of salt and base in case of basic buffer

$$pOH = pK_b$$

Q17. (e) Explain the term buffer capacity.

Buffer Capacity

"The capability of a buffer solution to resist the change in its pH when a small amount of acid or a base is added in it is called buffer capacity."

Explanation

It can be measured quantitatively that how much extra acid or base, the solution can absorb before the buffer is essentially destroyed. Buffer capacity of a buffer solution is determined by the sizes of actual molarities of its components. So, a chemist must decide before making the buffer solution, what outer limits of change in its pH can be tolerated.

Let us do some calculations to check the effectiveness of a buffer system. Consider that we have a buffer having 0.11 molar CH_3COONa and 0.09 molar acetic acid. Its pH will be 4.83.

$$pH = pKa + \log\frac{[salt]}{[acid]}$$

$$pH = 4.74 + \log\frac{0.11}{0.09}$$

$$pH = 4.74 + 0.087 = 4.83$$

Let us add 0.01 moles of NaOH in one dm^3 of the buffer solution. Addition of 0.01 moles NaOH per dm^{-3} of solution will change the pH from 7.00 to 12.00 in pure water. Since, NaOH is a strong base and it is 100% dissociated, it generates 0.01 moles of OH^{-1} ions.

$$\underset{0.01\ mol\ dm^{-3}}{NaOH} \longrightarrow \underset{0.01\ mol.dm^{-3}}{Na^+} + \underset{0.01\ mol.dm^{-3}}{OH^-}$$

Out of 0.09 mole of CH_3COOH, 0.01 mole will react with OH^- and 0.08 moles of CH_3COOH is left behind in one dm^{-3} of solution. This neutralization, of course, makes the identical change in the amount of CH_3COONa and its concentration will increase from 0.11 mole to 0.12 mole.

Henderson's equation

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

Putting the new concentrations of salt and acid after addition of NaOH.

$$pH = pK_a + \log\frac{0.12}{0.08}$$
$$= 4.74 + \log 1.5$$
$$= 4.74 + 0.176$$
$$pH = 4.92$$

Conclusion

It means that there is a very small change in pH from 4.83 to 4.92 that is only a difference of 0.1. So we reach the conclusion that a buffer does not hold the pH exactly constant. But it does a very good job in limiting the change in pH to a very small amount.

Q8. (a) What is the solubility product? Derive the solubility product expression for sparingly soluble compounds, $AgCl, Ag_2CrO_4$, and $PbCl_2$.

EQUILIBRIA OF SLIGHTLY SOLUBLE IONIC COMPOUNDS (SOLUBILITY PRODUCT)

"The product of the equilibrium concentration of ions raised to an exponent equal to the coefficient of the balanced equation at given temperature is called solubility product (K_{sp})."

Mathematical form

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

$$K_c = \frac{[A^{+y}]^x[B^{-x}]^y}{[A_xB_y]}$$

$$K_c[A_xB_y] = [A^{+y}]^x[B^{-x}]^y$$

$$K_{sp} = [A^{+y}]^x[B^{-x}]^y$$

- K_{sp} is the product of molar solubilities of two ions at equilibrium.
- K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent.
- The value of K_{sp} is a measure of how far to the right dissolution proceeds at equilibrium i.e. saturation.

Examples

1. When $PbCl_2$ is shaken with water the solution contains Pb^{+2}, Cl^- and un-dissociated $PbCl_2$. It means an equilibrium exists between $PbCl_2$ (solid solute) and the dissolved ions, Pb^{+2} and Cl^-.

$$PbCl_{2(s)} \rightleftharpoons PbCl_{2(aq)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Cl^-_{(aq)}$$

According to law of mass action:

$$K_c = \frac{[Pb^{+2}][Cl^-]^2}{[PbCl_2]}$$

$$K_c[PbCl_2] = [Pb^{+2}][Cl^-]^2$$

$$K_{sp} = [Pb^{+2}][Cl^-]^2 = 1.6\times10^{-5} \text{ at } 25°C$$

2. Lead sulphate $PbSO_4$ is a well-known sparingly soluble compound and it dissociates to a very small extent.

$$PbSO_{4(s)} \rightleftharpoons PbSO_{4(aq)} \rightleftharpoons Pb^{+2}_{(aq)} + SO^{-2}_{4(aq)}$$

According to law of mass action:

$$K_c = \frac{[Pb^{+2}][SO_4^{-2}]}{[PbSO_4]}$$

Being a sparingly soluble salt, the concentration of $PbSO_4$ almost remains constant. Bring $[PbSO_4]$ on left hand side with K_c

$$K_c[PbSO_4] = [Pb^{2+}][SO_4^{2-}]$$

$$K_c[PbSO_4] = K_{sp}$$

$K_{sp} = [Pb^{2+}][SO_4^{2-}] = 1.6 \times 10^{-8}$ at 25°C

K_{sp} values for some ionic compounds (compounds are arranged alphabetically)

Salt	Ion Product	K_{sp}	Salt	Ion Product	K_{sp}
AgBr	$[Ag^+][Br^-]$	5.0×10^{-13}	CuS	$[Cu^{2+}][S^{2-}]$	8×10^{-34}
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	8.1×10^{-12}	FeS	$[Fe^{2+}][S^{2-}]$	6.3×10^{-18}
AgCl	$[Ag^+][Cl^-]$	1.8×10^{-10}	Fe_2S_3	$[Fe^{3+}]^2[S^{2-}]^3$	1.4×10^{-85}
AgI	$[Ag^+][I^-]$	8.3×10^{-17}	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	1.6×10^{-39}
Ag_2S	$[Ag^+]^2[S^{2-}]$	8×10^{-48}	HgS	$[Hg^{2+}][S^{2-}]$	2×10^{-50}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	3×10^{-34}	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	3.5×10^{-8}
$BaCO_3$	$[Ba^{2+}][CO_3^{2-}]$	2×10^{-9}	$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2$	6.3×10^{-10}
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	1.1×10^{-10}	MnS	$[Mn^{2+}][S^{2-}]$	3×10^{-11}
CdS	$[Cd^{2+}][S^{2-}]$	8.0×10^{-27}	$PbCl_2$	$[Pb^{2+}][Cl^-]^2$	1.6×10^{-5}
$CaCO_3$	$[Cd^{2+}][CO_3^{2-}]$	3.3×10^{-9}	$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}]$	2.3×10^{-13}
CaF_2	$[Ca^{2+}][F^-]^2$	3.2×10^{-11}	$PbSO_4$	$[Pb^{2+}][SO_4^{2-}]$	1.6×10^{-8}
$Ca(OH)_2$	$[Ca^{2+}][OH^-]^2$	6.5×10^{-6}	PbS	$[Pb^{2+}][S^{2-}]$	8.0×10^{-28}

APPLICATIONS OF SOLUBILITY PRODUCT

Q18. (b) How do you determine the solubility product of a substance when its solubility is provided in grams/100 g of water?

(1) Determination of K_{sp} from Solubility

From the solubility we can calculate the K_{sp} of salt. The solubility for most of the compounds are given in terms of the grams of the solute per 100 g of water. Since, the quantity of solute is very small, so 100 g of water solution is considered to be 100 ml of solution. The reason is that the density of water is very close to unity. Hence, we get the concentration in moles.dm^{-3} The number of moles of solute dm^{-3} of the solution is calculated by dividing the mass of the solute by its molar mass Then by using the balanced equation, we calculate the molarity of each ion and then K_{sp}.

Example: **The solubility of PbF_2 at 25°C is 0.64 gdm^{-3}. Calculate K_{sp} of PbF_2.**

Solution:

First of all convert the concentration from gdm^{-3} to moles dm^{-3}.

Mass of PbF_2 dissolved dm^{-3} = 0.64 g

Molecular mass of PbF_2 = 245.2 g mol^{-1}

$$\text{Number of moles of } PbF_2 = \frac{0.64\,\text{gdm}^{-3}}{245.2\,\text{gmol}^{-1}} = 2.6\times10^{-3}$$

The balanced equation for dissociation of PbF_2 is,

$$PbF_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2F^-_{(aq)}$$

2.6×10^{-3}M 0 + 0 t = 0 sec

"zero" moles 2.6×10^{-3} moles + $2\times2.6\times10^{-3}$ moles t = equilibrium

The expression of K_{sp} is

$$K_{sp} = [Pb^{2+}][F^-]^2$$

Putting values of concentration

$$K_{sp} = 2.6\times10^{-3}\times(2\times2.6\times10^{-3})^2 = 7.0\times10^{-8}$$

Q18. (c) How do you calculate the solubility of a substance from the value of solubility product?

(2) Determination of Solubility from K_{sp}

For this purpose, we need the formula of the compound and K_{sp} value. Then the unknown molar solubility S is calculated and the concentration of the ions are determined.

Example: **$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6} Calculate the solubility of $Ca(OH)_2$**

Solution: Let the solubility is represented by S in terms of moles dm^{-3}

The balanced equation is

$$Ca(OH)_2 \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

$$Ca(OH)_2 \rightleftharpoons 0 + 0 \quad \text{Initial stage}$$

$$Ca(OH)_2 \rightleftharpoons S + 2S \quad \text{Equilibrium stage}$$

The $K_{sp} = 6.5\times10^{-6}$

The concentration of OH^- is doulbe the concentration of Ca^{2+}, so

$$K_{sp} = [Ca^{2+}][OH^-]^2 = S\times(2S)^2$$

$$4S^3 = 6.5\times10^{-6}$$

$$\text{So, } S = \left(\frac{6.5\times10^{-6}}{4}\right)^{1/3} = (1.625\times10^{-6})^{1/3}$$

$$S = (1.625)^{1/3}\times10^{-2}$$

$$S = 1.175\times10^{-2}$$

Hence, at equilibrium stage 1.175×10^{-2} moles dm^{-3} of Ca^{2+} and $2\times1.175\times10^{-2} = 2.75\times10^{-2}$ moles dm^{-3} OH^- are present in the solution. In this way, we have calculated the individual concentrations of Ca^{+2} and OH^- ion from the solubility product of $Ca(OH)_2$

Relationship between K_{sp} and the solubility of some compounds

Formula	Number of ions	Cation Anion	K_{sp}	Solubility gdm^{-3}
$MgCO_3$	2	1/1	3.61×10^{-8}	1.9×10^{-4}
$PbSO_4$	2	1/1	1.69×10^{-8}	1.3×10^{-4}
$BaCrO_4$	2	1/1	1.96×10^{-10}	1.4×10^{-5}

$Ca(OH)_2$	3	1/2	6.5×10^{-6}	1.175×10^{-2}
BaF_2	3	1/2	1.35×10^{-5}	7.2×10^{-3}
CaF_2	3	1/2	3.2×10^{-11}	2.0×10^{-4}
Ag_2CrO_4	3	2/1	2.6×10^{-12}	8.7×10^{-5}

Effect of Common Ion on Solubility

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)}$$

Now add Na_2CrO_4, which is a soluble salt. CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

Key Points

1. The reversible chemical reactions can achieve a state in which the forward and the reverse processes are occurring at the same rate. This state is called state of chemical equilibrium. The concentrations of reactants and products are called equilibrium concentrations and the mixture is called equilibrium mixture.
2. Law of mass action provides the relationship among the concentrations of reactants and products of a system at equilibrium stage. The ratio of concentrations of the products to the concentrations of reactants is called equilibrium constant. The equilibrium constants are expressed as K_c, K_p, K_n and k_x.
3. The value of equilibrium constant can predict the direction and extent of a chemical reaction.
4. The effect of change of concentration, temperature, pressure or catalyst in a reaction can be studied with the help of Le-Chatelier's principle. Increasing concentrations of reactants or decreasing concentrations of products or heating of the endothermic reactions shifts the reaction to the forward direction. The change of temperature distubrbs the equilibrium position and the equilibrium constant of reaction. A catalyst decreases the time to reach the equilibrium and does not alter the equilibrium position and equilibrium constant under the given conditions.
5. Water is a very weak electrolyte and ionizes to a slight degree. The extent of this a auto ionization is expressed by ionic product of water called K_w, having a value 10^{-14} at 25°C. The addition of an acid or a base changes the $[H^+]$ and $[OH^-]$, but the ionic product remains the same at 25°C.
6. The concentration of H^+ is expressed in terms of pH and that of $[OH^-]$ in terms of pOH. Neutral water has a pH = 7 and pOH=7. The value of pK_w is 14 at 25°C.
7. According to Lowry-Bronsted concept of an acid and a base the conjugate base of a acid is always weak. So $pK_a + pK_b = pK_w$
   Where pK_a and pK_b are the parameters to measure the strength of acids and bases.
8. Those solutions which resist the change of pH are called buffer solutions. Buffer solutions of pH below 7 are prepared by mixing a weak acid and salt of it with strong base while basic buffers can be prepared by combining a weak base and salt of it with a strong acid. Hendersen's equation guides us quantitatively to have the buffer solutions of good buffer capacity and to select the pair of compounds for this purpose.
9. The solubility of sparingly soluble substances are calculated from the solubility product data. This data provides us the information about the selective precipitation and fractional precipitation
10. Common ion effect operates best in buffer solutions, and purification of certain substances. It is one of the best applications of Le-Chatelier's principle.

SOLVED OBJECTIVE EXERCISE

Q1: **Multiple choice questions:**

(i) For which system does the equilibrium constant, K_c has a units of (concentration)$^{-1}$?

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (b) $H_2 + I_2 \rightleftharpoons 2HI$

(c) $2NO_2 \rightleftharpoons N_2O_4$ (d) $2HF \rightleftharpoons H_2 + F_2$

(ii) Which statement about the following equilibrium is correct

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H = -188.3$ KJ mol^{-1}.

(a) the value of K_p falls with rise in temperature

(b) the value of K_p falls with increases in pressure

(c) adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide

(d) the value of K_p is equal to K_c

(iii) The pH of 10^{-3} mol dm^{-3} of an aqueous solution of H_2SO_4 is:

(a) 3.0 (b) 2.7

(c) 2.0 (d) 1.5

(iv) Solubility product of AgCl is 2.0×10^{-10} mol^2 dm^{-6} Maximum concentration of Ag^{+1} ions in the solution is:

(a) 2.0×10^{-10} mol dm^{-3} (b) 1.4×10^{-5} mol dm^{-3}

(c) 1.0×10^{-10} mol dm^{-3} (d) 4.0×10^{-20} mol dm^{-3}

(v) An excess of aqueous silver nitrate is added to aqueous barium chloride and precipitate is removed by filtration What are main ions in the filtrate:

(a) Ag^+ and NO_3^{-1} only (b) Ag^+ and Ba^{+2} and NO_3^{-1}

(c) Ba^{+2} and NO_3^{-1} only (d) Ba^{+2} and NO_3^{-1} and Cl^{-1}

Solved Exercise MCQ's

Q No	Answer	Reason
(i)	(c) $2NO_2 \rightleftharpoons N_2O_4$	• If the number of moles of reactants and products are equal, then Kc has no units as in (b) and (d). • $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ 4 mol 2 mol $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[mol\ dm^{-3}]^2}{[mol\ dm^{-3}][mol\ dm^{-3}]^3} = mol^{-2}\ dm^{6}$ • $2NO_2 \rightleftharpoons N_2O_4$ $K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{[mol\ dm^{-3}]}{[mol\ dm^{-3}]^2} = mol^{-1}\ dm^{3}$ Or (concentration)$^{-1}$
(ii)	(a) the value of K_p falls with rise in temperature	According to Le – Chaletier's principle: If a reaction is exothermic, by increasing the temperature at equilibrium state, the equilibrium will shift towards left and product will convert into reactants. As a result the concentration of products decreases which falls the Kc.
(iii)	(b) 2.7	$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{-2}$ $[H^+] = 2 \times 10^{-3}$

		pH $= -\log[H^+]$ $= -\log 2\times10^{-3} = -(\log 2 - 3\log 10) = -(0.301 - 3)$ pH $= 2.67$ Or 2.7
(iv)	(b) 1.4×10^{-5} mol dm^{-3}	$AgCl \rightleftharpoons Ag^{+1} + Cl$ $Ksp = [Ag^{+1}][Cl^{-1}]$ $2.0 \times 10^{-10} = [Ag^{+1}][Cl^{-1}]$ Since $[Ag^{+1}] = [Cl^{-1}]$ $2.0 \times 10^{-10} = [Ag^{+1}]^2$ $\sqrt{2.0\times10^{-10}} = \sqrt{[Ag^{+1}]^2}$ $[Ag^{+1}] = 1.414 \times 10^{-5}$ mol dm^{-3}
(v)	(b) Ag^+ and Ba^{+2} and NO_3^{-1}	$2AgNO_3 + BaCl_2 \longrightarrow 2AgCl + Ba(NO_3)_2$ Since AgCl is insoluble in water, so it precipitates out. $AgNO_3$ is in excess. Some mass of it used in the formation of AgCl while remaining left behind. Hence filtrate contains Ag^+ and Ba^{+2} and NO_3^{-1}.

Q2: Fill in the blanks:

(i) Law of mass action states that the ________ at which a reaction precedes is directly proportional to the product of active masses of ________.

(ii) In an exothermic reversible reaction, ________ temperature will shift equilibrium towards the forward direction.

(iii) The equilibrium constant for a reaction $2O_3 \rightleftharpoons 3O_2$ is 10^{55} at 25° C, it tells that ozone is ________ at room temperature.

(iv) In a gas phase reaction, if the number of moles of reactants are equal to the number of moles of product, K_c of reaction is ________ to the K_p.

(v) Buffer solution is prepared by mixing together a weak base, and its salt with ________ or a weak acid and its salt with ________.

ANSWERS

(i) rate of reaction, reactants	(ii) low
(iii) unstable	(iv) equal
(v) strong acid, strong base	

Q 3: Label the sentences as true or False:

(i) When a reversible reaction attains equilibrium both reactants and products are present in the reaction mixture.

(ii) The K_c for the reaction $A + B \rightleftharpoons C + D$ is given as $K_c = \frac{[C][D]}{[A][B]}$ so it is assumed that $[A] = [B] = [C] = [D]$.

(iii) A catalyst is a compound which speeds up reaction and consequently increases yield of product.

(iv) Ionic product K_w of pure water at 25°C is 10^{-14} mol^2 dm^{-6} and is represented by an expression $K_w = [H^+][OH^-] = 10^{-14}$ mol^2 dm^{-6}.

(v) AgCl is sparingly soluble ionic solid in water. Its solution contains excess of Ag^+ and Cl^- ions

ANSWERS

(i) True	(ii) False	(iii) False	(iv) True	(v) False

SHORT ANSWERS TO EXERCISE

Q4. (c) Write K_c for the following reactions:

(i) $Sn^{+2}_{(aq)} + 2Fe^{+3}_{(aq)} \rightleftharpoons Sn^{+4}_{(aq)} + 2Fe^{+2}_{(aq)}$

$$K_c = \frac{[Product]}{[Reactants]} = \frac{[Sn^{+4}][Fe^{+2}]^2}{[Sn^{+2}][Fe^{+3}]^2}$$

(ii) $Ag^{+}_{(aq)} + Fe^{+2}_{(aq)} \rightleftharpoons Fe^{+3}_{(aq)} + Ag^{\circ}$

$$K_c = \frac{[Fe^{+3}][Ag^{\circ}]}{[Ag^{+}][Fe^{+2}]}$$

(iii) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

(iv) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

$$K_c = \frac{[H_2O]^6[NO]^4}{[NH_3]^4[O_2]^5}$$

(v) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Q5. (a) Write down K_c for the following reversible reactions. Suppose that the volume of reaction mixture in all the cases is "V" dm^3 at equilibrium state.

(i) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

moles at t = o "a" mol "b" mol $\rightleftharpoons$ "o" mol "o" mol

moles at t = equilibrium $(a - x) + (b - x) \rightleftharpoons (x) + (x)$

conc in mol / v (dm^3) so $\left(\frac{a-x}{v}\right) + \left(\frac{b-x}{v}\right) \rightleftharpoons \left(\frac{x}{v}\right) + \left(\frac{x}{v}\right)$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = \frac{\left(\frac{x}{v}\right)\times\left(\frac{x}{v}\right)}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$K_c = \frac{x^2}{v^2} \times \frac{v^2}{(a-x)(b-x)}$$

$$\text{so } K_c = \frac{x^2}{(a-x)(b-x)}$$

(ii) $H_2 + I_2 \rightleftharpoons 2HI$

moles at t = 0 — "a" mol + "b" mol $\rightleftharpoons$ "o" mol

at t = equilibrium — $(a-x) + (b-x) \rightleftharpoons 2x$

conc. mole/dm³ so — $\left(\frac{a-x}{v}\right)+\left(\frac{b-x}{v}\right) \rightleftharpoons \frac{2x}{v}$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$K_c = \frac{4x^2}{(a-x)(b-x)}$$

(iii) $2HI \rightleftharpoons H_2 + I_2$

t = 0 — a mole $\rightleftharpoons$ 0 + 0

t = equilibrium — $(a-2x) \rightleftharpoons x + x$

$$\left(\frac{a-2x}{v}\right) \rightleftharpoons \left(\frac{x}{v}\right)+\left(\frac{x}{v}\right)$$

$$K_c = \frac{[Products]}{[Reactant]}$$

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{\left(\frac{x}{v}\right)\times\left(\frac{x}{v}\right)}{\left(\frac{a-2x}{v}\right)^2}$$

$$K_c = \frac{x^2}{(a-2x)^2}$$

(iv) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

moles at t = 0 — $a \rightleftharpoons 0 + 0$

moles at t = equilibrium — $(a-x) \rightleftharpoons x + x$

concentration in moles/'V'dm³ — $\left(\frac{a-x}{v}\right) \rightleftharpoons \left(\frac{x}{v}\right)+\left(\frac{x}{v}\right)$

$$K_c = \frac{[Product]}{[Reactant]}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{v}\times\frac{x}{v}}{\left(\frac{a-x}{v}\right)}$$

$$K_c = \frac{x^2}{v(a-x)}$$

(v) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

moles at t = 0 — $a + b \rightleftharpoons 0$

moles at t = equilibrium — $(a-x) + (b-3x) \rightleftharpoons 2x$

concentration in moles/'V' dm³ — $\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right) \rightleftharpoons \frac{2x}{v}$

$$K_c = \frac{[Product]}{[Reactant]}$$

$$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

So $$K_c = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3}$$

$$K_c = \frac{4x^2v^2}{(a-x)(b-3x)^3}$$

NUMERICAL OF EXERCISE

Q19. K_c value for the following reaction is 0.016 at 520°C.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Equilibrium mixture contains [HI] = 0.08 M, [H_2] = 0.01 M, [I_2] = 0.01 M. To this mixture more HI is added so that its new concentration is 0.096 M. What will be the concentrations of [HI], [H_2], [I_2] when equilibrium is re-established.

Ans. **Given data:**

Initial concentration of HI = 0.08 M

Initial concentration of H_2 = 0.01 M

Initial concentration of I_2 = 0.01 M

New concentration of HI = 0.096 M

Requirement:

[HI], [H_2] and [I_2] = ?

Solution:

$$2HI \rightleftharpoons H_2 + I_2$$

Initial concentration

$$0.08\ M \rightleftharpoons 0.01\ M + 0.01\ M$$

At equilibrium, the new concentrations

$$(0.096 - 2x) \rightleftharpoons (0.01 + x) + (0.01 + x)$$

$$K_c = \frac{\text{concentration of product}}{\text{concentration of reactants}} = \frac{[H_2][I_2]}{[HI]^2}$$

$$0.016 = \frac{[0.01+x][0.01+x]}{[0.096-2x]^2}$$

$$0.016 = \frac{(0.01 + x)^2}{(0.096 - 2x)^2}$$

Taking square root on both sides

$$\sqrt{0.016} = \sqrt{\frac{(0.01 + x)^2}{(0.096 - 2x)^2}}$$

$$0.126 = \frac{0.01 + x}{0.096 - 2x}$$

$$0.126(0.096 - 2x) = 0.01 + x$$

$$0.012096 - 0.252x = 0.01 + x$$

$$0.012096 - 0.01 = x + 0.252x$$

$$0.002096 = 1.252x$$

$$x = \frac{0.002096}{1.252}$$

$$x = 1.68 \times 10^{-3} M \quad \text{or} \quad 0.00168\ M$$

Concentrations at equilibrium can be calculated as follows

(i) $[HI] = (0.096 - 2x)$
$= 0.096 - 2 \times 0.00168$
$= 0.096 - 0.00336$
$= 0.09264\ M$

(ii) $[H_2] = 0.01 + x$
$= 0.01 + 0.00168$
$= 0.01168\ M$

(iii) $[I_2] = 0.01 + x$
$= 0.01 + 0.00168$
$= 0.01168\ M$

$[HI] = 0.0926\ M$
$[H_2] = 001168\ M$
$[I_2] = 0.01168\ M$

Q20. The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4. A mixture of 3 moles CH_3COOH, and one mole C_2H_5OH is allowed to attain equilibrium. Calculate amount of ethyl acetate present at equilibrium in number of moles and grams. Also calculate masses of reactants left behind.

Ans. **Given data:** $K_c = 4$

Moles of acetic acid = 3

Moles of ethyl alcohol = 1

Requirement:

Moles of ethyl acetate = ? Amount of ethyl acetate = ?

Moles of acid = ? Amount of acid in gram = ?

Moles of alcohol = ? Amount of alcohol in gram = ?

Solution:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

at t = 0: 3 mol + 1 mol ⇌ 0 mol + 0 mol

at t = equilibrium: (3 − x) mol + (1 − x) mol ⇌ (x) mol + (x) mol

$$K_c = \frac{[\text{Product}]}{[\text{Reactants}]} = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$4 = \frac{(x)(x)}{(3 - x)(1 - x)} = \frac{x^2}{x^2 - 4x + 3}$$

$$x^2 = 4(x^2 - 4x + 3)$$

$$x^2 = 4x^2 - 16x + 12$$

$$4x^2 - x^2 - 16x + 12 = 0$$

$$3x^2 - 16x + 12 = 0$$

It is a quadratic equation. To evaluate the value of x, the formula used is:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Let us consider that [a = 3, b = −16, c = 12] for above reaction

Thus $$x = \frac{-(16) \pm \sqrt{(16)^2 - 4 \times 3 \times 12}}{2 \times 3}$$

$$= \frac{16 \pm \sqrt{256 - 144}}{6}$$

$$= \frac{16 \pm \sqrt{112}}{6} = \frac{16 \pm 10.58}{6}$$

so $$x = \frac{16 + 10.58}{6} = 4.43 \text{ moles or}$$

$$x = \frac{16 - 10.58}{6} = 0.903 \text{ moles}$$

From the above two values of x

$x \neq 4$ as initial concentration of CH_3COOH is less i.e., 3 moles. So value of x = 0.903 moles.

(i) Concentration of (CH_3COOH) at equilibrium
$= 3 - x = 3 - 0.903 = 2.097$ moles

(ii) Concentration of (C_2H_5OH) at equilibrium
$= 1 - x = 1 - 0.903 = 0.097$ moles

(iii) Concentration of ethyl acetate = x = 0.903 moles

(iv) Mass = Moles × Mol. mass

(a) Amount of $CH_3COOH = 2.097 \times 60 = 125.82$ g

(b) Amount of $C_2H_5OH = 0.1 \times 46 = 4.6$ g

(c) Amount of ethyl acetate = 0.9 × 88 = 79.46 g

Moles of ethyl acetate = 0.9 moles
Mass of ethyl acetate = 79.46 g
Mass of acid left behind = 126 g
Mass of alcohol left = 4.6 g

Q21. Study the equilibrium

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

When 1.00 mol of steam and 1 mol of CO are allowed to react and reach to equilibrium 33.3% of equilibrium mixture is hydrogen. Calculate the value of K_p. State the units of K_p.

Ans. **Given data:**

Moles of steam = 1.00

Moles of CO = 1.00

% of H_2 at equilibrium = 33.3%

Requirement:

(i) Value of K_p = ?

(ii) Unit of K_p = ?

Solution:

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

concentration at t = 0 $\quad$ (1.00) mole + (1.00) mole $\rightleftharpoons$ 0 + 0

concentration at t = eq $\quad$ (1 − x) mole + (1 − x) mole $\rightleftharpoons$ x + x

Total moles of reaction mixture = 1 + 1 = 2 mol.

Moles of H_2 at equilibrium = 33.3%

It means that $\frac{x}{2} = \frac{\text{conc. of } H_2}{100}$

$$\frac{x}{2} = \frac{33.3}{100}$$

$$x = \frac{2 \times 33.3}{100} = 0.666 \text{ moles}$$

So $[H_2O] = 1 - x$

$= 1 - 0.666 = 0.333$ moles

$[CO] = 1 - x$

$= 1 - 0.666 = 0.333$ moles

$[H_2] = [CO_2] = x = 0.666$ moles

$K_p = K_c(RT)^{\Delta n}$

as $\Delta n = 0$ so

$K_p = K_c$

$$K_p = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{0.666 \times 0.666}{0.333 \times 0.333}$$

$K_p = 4$

$$\text{Units of } K_p = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{\text{mol dm}^{-3}.\text{ mol dm}^{-3}}{\text{mol dm}^{-3}.\text{ mol dm}^{-3}}$$

= no unit

$K_p = 4$

K_p has no unit

Q22. (a) Calculate the pH of 10^{-4} mol dm^{-3} of HCl.

Ans. **Given data:**

concentration of HCl = 10^{-4} mol dm^{-3}

Requirement:

pH of HCl = ?

Solution:

$HCl \rightleftharpoons H^+ + Cl^-$ (ionization)

If $\quad$ (1) mole $\rightleftharpoons$ (1) mole + (1) mole

Then $\quad 10^{-4}$ mol dm^{-3} $\rightleftharpoons$ 10^{-4} mol dm^{-3} + 10^{-4} mol dm^{-3}

So $\quad [H^+] = 10^{-4}$ mol dm^{-3}

pH $= -\log[H^+]$

$= -\log 10^{-4}$

pH = 4

Q22. (b) Calculate the pH of 10^{-4} mol dm^{-3} of $Ba(OH)_2$

Ans. **Given data:**

concentration of $Ba(OH)_2 = 10^{-4}$ mol dm^{-3}

Requirement:

pH of $Ba(OH)_2$ = ?

Solution:

$Ba(OH)_2 \rightleftharpoons 2OH^- + Ba^{+2}$

If $\quad$ (1) mole $\rightleftharpoons$ 2 mole + (1) mole

Then $\quad 10^{-4}$ mol dm^{-3} $\rightleftharpoons$ 2×10^{-4} mol dm^{-3} + 10^{-4} mol dm^{-3}

So $\quad [OH^-] = 2 \times 10^{-4}$ mol dm^{-3}

pOH $= -\log[OH^-]$

$= -\log[2 \times 10^{-4}]$

$= 3.698$

pH + pOH = 14

pH = 14 − pOH

pH = 14 − 3.698 = 10.302

Q22. (c) Calculate the pH of 1 mol dm^{-3} of H_2X which is 50% ionized.

Ans. **Given data:**

concentration of H_2X = 1 mol dm^{-3}

Ionization = 50%

Requirement:

pH of H_2X = ?

Solution:

$H_2X \rightleftharpoons 2H^+ + X^-$ (if 100% is its ionization)

moles $\quad 1 \rightleftharpoons 2 + 1$

But as 50% dissociation is there.

So $\quad$ 1 mole of H_2X gives mol of H^+ = 1 mole

$[H^+] = 1$ mol dm^{-3}

pH $= -\log[H^+]$

$= -\log[1]$

pH = 0

Q22. (d) Calculate the pH of 1 mol dm^{-3} NH_4OH which is 1% dissociated.

Ans. **Given data:**

Ionization of NH_4OH = 1%

concentration of NH_4OH = 1 mol dm^{-3}

Requirement:

pH of NH_4OH = ?

Solution:

$NH_4OH \rightleftharpoons OH^- + NH_4^+$

(100% ionization) (1) mole $\rightleftharpoons$ (1) mole + (1) mole

(1% ionization) (1) mole $\rightleftharpoons$ 0.01 + 0.01 (mol)

So $[OH^-] = 0.01\ mol\ dm^{-3}$

$pOH = -\log[OH^-] = -\log 0.01$

$= 2$

$pH + pOH = 14$

$pH = 14 - pOH$

$= 14 - 2$

$pH = 12$

Q23. (a) Benzoic acid C_6H_5COOH is a weak mono-basic acid $K_a = 6.4 \times 10^{-5}\ mol\ dm^{-3}$. What is the pH of the buffer containing 7.2 g of sodium benzoate and 0.02 mol benzoic acid.

Ans. **Given data:**

$K_a = 6.4 \times 10^{-5}\ mol\ dm^{-3}$

$[C_6H_5COOH] = 0.02\ mol\ dm^{-3}$

$[C_6H_5COONa] = 7.2\ g$

Requirement:

pH of Buffer = ?

Solution:

Using Handerson's equation

$$pH = pK_a + \log\frac{[Salt]}{[acid]}$$

We need moles of C_6H_5COONa:

Mol. mass of $C_6H_5COONa = 144\ g\ mol^{-1}$

$$\text{No. of moles} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{7.2}{144} = 0.05\ mol\ dm^{-3}$$

Applying Handerson's equation

$$pH = pK_a + \log\frac{[0.05]}{[0.02]} \qquad \therefore [pK_a = -\log K_a]$$

$$= -\log 6.4\times10^{-5} + \log\frac{0.05}{0.02}$$

$$= 4.19 + 0.39$$

$pH = 4.58$

Q23. (b) A buffer solution has been prepared by mixing 0.2 M CH_3COONa and 0.5 M CH_3COOH in 1 dm^3 of solution. Calculate the pH of solution. pK_a of acid = 4.74 at 25°C. How the values of pH will change by adding 0.1 mole of NaOH and 0.1 mole of HCl respectively.

Ans. **Given data:**

$[CH_3COOH] = 0.5\ M$

$[CH_3COONa] = 0.2\ M$

pK_a of acid = 4.74 at 25°C

Requirement:

(i) pH = ?

(ii) Change in pH by adding base

(iii) Change in pH by adding acid

Solution:

(i) According to Handerson's equation

$$pH = pK_a + \log\frac{[Salt]}{[acid]}$$

$$= 4.74 + \log\frac{[0.2]}{[0.5]} = 4.74 + \log 0.4$$

$pH = 4.74 - 0.39 = 4.35$

(ii) Change in pH by adding 0.1 M NaOH:

It results in an increase in concentration of salt and decrease in that of an acid so

New data:

$[CH_3COOH] = 0.5 - 0.1 = 0.4\ M$

$[CH_3COONa] = 0.2 + 0.1 = 0.3\ M$

$$pH = pK_a + \log\frac{[Salt]}{[acid]}$$

$$= 4.74 + \log\frac{0.3}{0.4}$$

$$= 4.74 - 0.12$$

$pH = 4.62$

(iii) Change in pH by adding 0.1 M HCl:

It results in a decrease in concentration of salt and increase in concentration of H^+ ions of acid

New data:

$[CH_3COOH] = 0.5 + 0.1 = 0.6\ M$

$[CH_3COONa] = 0.2 - 0.1 = 0.1\ M$

$$pH = pK_a + \log\frac{[Salt]}{[acid]}$$

$$= 4.74 + \log\frac{[0.1]}{[0.6]}$$

$$= 4.74 - 0.778$$

$$= 3.962$$

pH of Buffer = 4.35

pH after adding 0.1 M HCl = 3.962

pH after adding 0.1 M NaOH = 4.62

Q24. The solubility of CaF_2 in water at 25°C is found to be $2.05 \times 10^{-4}\ mol\ dm^{-3}$. What is the value of K_{sp} at this temperature.

Ans. **Given data:**

Solubility of $CaF_2 = 2.05 \times 10^{-4}\ mol\ dm^{-3}$ at 25°C

Requirement:

$$CaF_2 \rightleftharpoons Ca^{+2}_{(aq)} + 2F^{-1}_{(aq)}$$

$$1\ mol \rightleftharpoons 1\ mol + 2\ mol$$

$$2.05\times10^{-4}\ mol\ dm^{-3} \rightleftharpoons 2.05\times10^{-4}\ mol\ dm^{-3} + 2\times2.05\times10^{-4}\ mol\ dm^{-3}$$

$K_{sp} = [Cation][Anion]$

$K_{sp} = [Ca^{+2}][F^-]^2$

$= [2.05\times10^{-4}][2\times2.05\times10^{-4}]^2$

$= [2.05\times10^{-4}][4.1\times10^{-4}]^2$

$= 3446 \times 10^{-11}$

K_{sp} of $CaF_2 = 3.446 \times 10^{-11}$

Q25. Solubility product of Ag_2CrO_4 is 2.6×10^{-2} at 25°C. Calculate the solubility of this compound.

Ans. **Given data:**

K_{sp} of $Ag_2CrO_4 = 2.6 \times 10^{-2}$ at 25°C

Requirement:

Solubility of Ag_2CrO_4 = ?

[redacted]

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+_{(aq)} + CrO^{-2}_{4(aq)}$$

Let the solubility of salts is supposed as 'S' so

$$S \rightleftharpoons 2S + S$$

$K_{sp} = [Ag^+]^2[CrO_4^{-2}]$

$= (2S)^2(S)$

$2.6 \times 10^{-2} = 4S^3$

$S^3 = \dfrac{2.6\times10^{-2}}{4} = 6.5\times10^{-3}$

$\sqrt[3]{S^3} = \sqrt[3]{6.5\times10^{-3}}$

$S = 0.1866 \text{ mol dm}^{-3}$

Solubility of Ag_2CrO_4 = 0.1866 mol dm^{-3}

SOLVED EXAMPLES

Example (1):

The following reaction was allowed to reach the state of equilibrium

$$2A_{(aq)} + B_{(aq)} \rightleftharpoons C_{(aq)}$$

The initial amounts of the reactants present in one dm^3 of solution were 0.50 mole of A and 0.60 mole of B. At equilibrium the amounts were 0.20moles of A and 0.45 mole of B and 0.15 mole of C. Calculate the equilibrium constant K_c

Ans. **Given Data:**

Initial concentration of A = 0.50 moles

Initial concentration of B = 0.60 moles

Equilibrium concentration of A = 0.20 moles

Equilibrium concentration of B = 0.45 moles

Equilibrium concentration of C = 0.15 moles

Required:

Calculate equilibrium constant = K_c = ?

Solution:

Equation

$$2A_{(aq)} + B_{(aq)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C_{(aq)}$$

$$K_c = \frac{[C]}{[A]^2[B]}$$

	$2A_{(aq)}$	+ $B_{(aq)}$	$\rightleftharpoons C_{(aq)}$
Initial conc	(0.5) mol	(0.60) mol	(0.00) mol
Equilibrium conc	(0.20) mol	(0.45) mol	(0.15) mol

Since

$$K_c = \frac{[C]}{[A]^2[B]} = \frac{(0.15)}{(0.20)^2(0.45)}$$

$$K_c = \frac{1}{0.04 \times 3} = \frac{1}{0.12}$$

$K_c = 8.3$

The units have been ignored for the sake of convenience.

Example (2):

$N_{2(g)}$ and $H_{2(g)}$ combine to give $NH_{3(g)}$. The values of K_c in this reaction at 500°C is 6.0×10^{-2}. Calculate the value of K_p for this reaction.

Ans. **Given Data:**

$K_c = 6.0 \times 10^{-2}$

$T = 500°C + 273 = 773K$

Required:

Calculate the value of K_p = ?

Solution: **The reaction for the synthesis of ammonia is**

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

The relationship between K_p and K_c

$K_p = K_c (RT)^{\Delta n}$

Δn = Number of moles of products – Number of moles of reactants

$\Delta n = 2 - 4 = -2$

$R = 0.0821 \text{ dm}^3\text{atmK}^{-1}\text{ mole}^{-1}$

Substituting these values in the expression

$K_p = 6.0 \times 10^{-2} (773 \times 0.0821)^{-2}$

$= 6.0 \times 10^{-2} (63.5)^{-2}$

$K_p = \dfrac{6.0\times10^{-2}}{(63.5)^2} = 1.5 \times 10^{-5}$

$K_p = 1.5\times10^{-5}$

The value of K_p is smaller than K_c. Those reactions which take place with the increase in number of moles mostly have greater K_p than K_c.

Example (3):

Esterification reaction between ethanol and acetic acid was carried out by mixing definite amounts of ethanol and acetic acid along with some mineral acid as a catalyst. Sample was drawn out of the reaction mixture to check the progress of the esterification reaction. In one of the samples drawn after time (t), the conc. of the species were found to be $[CH_3COOH]$ = 0.025 mole dm^{-3}, $[C_2H_5OH]$ = 0.032 mole dm^{-3}, $[CH_3COOC_2H_5]$ = 0.02 mole dm^{-3}, and $[H_2O]$ = 0.04 mole dm^{-3}. Find out the direction of the reaction if K_c for the reaction at 25°C is 4

Ans. **Given Data:**

$[CH_3COOH] = 0.025 mol\ dm^{-3}$

$[C_2H_5OH] = 0.032\ mol\ dm^{-3}$

$[CH_3COOC_2H_5] = 0.05\ mol\ dm^{-3}$

$[H_2O] = 0.04 mol\ dm^{-3}$

$K_c = 4$ at 500 °C

Required:

Direction of the reaction = ?

Solution: Esterification reaction is represented by the following equation.

$$CH_3COOH + C_2H_5OH \xrightleftharpoons{H^+} CH_3COOC_2H_5 + H_2O$$

All the substance are present in same volume of the solution, therefore K_c is given by

$$\text{Ratio} = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Putting the values of conc., at time "t".

$$\text{Ratio} = \frac{0.05 \times 0.04}{0.025 \times 0.032} = 2.50$$

The given value of K_c for this reaction is 4 and 2.50 is less than K_c.

Therefore, The direction of the reaction will be forward to attain the equilibrium

---

Example (4):

What is the percentage ionization of acetic acid in a solution in which 0.1mole of it has been dissolved per dm^3 of the solution?

Ans. **Given Data:**

Initial concentration of acetic acid = $[CH_3COOH] = 0.1 mol\ dm^{-3}$

Required:

Percentage ionization of acetic acid = ?

Solution:

Equation

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad K_a = 1.85 \times 10^{-5}$$

Initial conc. 0.10mole 0 mole 0 mole t = 0 sec

Change in concentration due to ionization.

$(0.1 - x)$ mole $\rightleftharpoons$ x mole x mole t= Equilibrium

Concentration at equilibrium

$$(0.1 - x) \approx 0.10 \rightleftharpoons x\ mole + x\ mole$$

because the value of x is very small as compare to 0.1 the reason is that CH_3COOH is much weak electrolyte

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x \cdot x}{0.1}$$

Putting the value of K_a

$$1.85 \times 10^{-5} = \frac{x^2}{0.1}$$

or $x^2 = 1.85 \times 10^{-5} \times 0.1 = 1.85 \times 10^{-6}$

Taking square root on both sides

$$\sqrt{x^2} = \sqrt{1.85 \times 10^{-6}}$$

$$x = 1.3 \times 10^{-3} \text{ moles}$$

In other words $[H^+] = 1.3 \times 10^{-3}$ mole dm^{-3}

This is the amount of ionized acid

$$\%\text{age ionization} = \frac{\text{Concentration of ionized acid}}{\text{Original concentration}} \times 100$$

$$= \frac{1.3 \times 10^{-3}}{0.1} \times 100$$

$$= 1.3$$

Percentage ionization of acetic acid = 1.3

Example (5):

Calculate pH of a buffer solution in which 0.11 molar CH_3COONa and 0.09 molar acetic acid solutions are present. K_a for CH_3COOH is 1.85×10^{-5}

Ans. **Given Data:**

$[CH_3COONa] = 0.11M$

$[CH_3COOH] = 0.09M$

K_a of $CH_3COOH = 1.85 \times 10^{-5}$

Required:

pH of Buffer solution = ?

Solution:

$$pK_a = -\log K_a$$

$$= -\log 1.8 \times 10^{-5}$$

$$= 4.74$$

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$pH = 4.74 + \log\frac{0.11}{0.09}$$

$$pH = 4.74 + 0.087$$

$$pH = 4.83$$

Example (6):

The solubility of PbF_2 at 25°C is $0.64 gdm^{-3}$. Calculate K_{sp} of PbF_2.

Ans. **Given Data:**

Solubility of $PbF_2 = 0.64 gdm^{-3}$ at 25°C

Required:

K_{sp} = ?

Solution:

First of all convert the concentration from gdm^{-3} to moles dm^{-3}

Mass of PbF_2 dissolved dm^{-3} = 0.64g

Molecular mass of $PbF_2 = 207.2 + 19 \times 2$

$= 207.2 + 38 = 245.2$g/mole

$$\text{Number of moles of } PbF_2 = \frac{0.64\ gdm^{-3}}{245.2\ gmol^{-1}}$$

$= 2.6 \times 10^{-3}$ mole dm^{-3}

Balance Equation:

$PbF_{2(s)}$	$\rightleftharpoons$	$Pb^{+2}_{(aq)}$	+	$2F^{-1}_{(aq)}$	
2.6×10^{-3} mole dm^{-3}		0		0	at t = 0 Sec
Zero mole dm^{-3}		2.6×10^{-3} mole dm^{-3}		$2 \times 2.6 \times 10^{-3}$ moles dm^{-3}	t = eq

The expression of K_{sp} is

$$K_{sp} = [Pb^{+2}_{(aq)}][F^{-1}_{(aq)}]^2$$

Putting values of concentration

$$K_{sp} = (2.6 \times 10^{-3})(2 \times 2.6 \times 10^{-3})^2$$

$$K_{sp} = 7.0 \times 10^{-8} \text{ Answer}$$

Example (7):

$Ca(OH)_2$ is sparingly soluble compound. Its solubility constant is 6.5×10^{-6}. Calculate the solubility of $Ca(OH)_2$.

Ans. **Given Data:**

Solubility constant = $K_{sp} = 6.5 \times 10^{-6}$

Required:

Solubility of $Ca(OH)_2$ = ?

Solution:

Balance Equation

$$Ca(OH)_2 \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

Let us suppose

Solubility of $Ca(OH)_2$ = S

$Ca(OH)_2$	$\rightleftharpoons$	$Ca^{2+}_{(aq)}$	+	$2OH^-_{(aq)}$	
S		0		0	at t = 0 sec
S		S		2S	t = equilibrium

The concentration of OH^- is double than the concentration of Ca, so

$$K_{sp} = [Ca^{2+}_{(aq)}][OH^-_{(aq)}]^2$$

$$6.5 \times 10^{-6} = S \times (2S)^2$$

$$6.5 \times 10^{-6} = S \times 4S^2$$

$$6.5 \times 10^{-6} = 4S^3$$

$$4S^3 = 6.5 \times 10^{-6}$$

$$S^3 = \frac{6.5 \times 10^{-6}}{4}$$

$$S = \left(\frac{6.5 \times 10^{-6}}{4}\right)^{1/3}$$

$$S = (1.625 \times 10^{-6})^{1/3}$$

$$S = (1.625)^{1/3} \times 10^{-6 \times 1/3}$$

$$S = 1.175 \times 10^{-2}$$

Hence At equilibrium stage

$$S = [Ca^{+2}] = 1.175 \times 10^{-2} \text{ mole dm}^{-3}$$

$$[OH^-] = 2S = 2 \times 1.175 \times 10^{-2}$$

$$= 2.350 \times 10^{-2} \text{ mole dm}^{-3}$$

Concentration of Ca^{+2} ions = 1.175×10^{-2} mole dm^{-3}

Concentration of OH^- ions = 2.350×10^{-2} mole dm^{-3}

Additional Questions

Q. When the concentration of salt is increased in an acidic buffer than the pH of the solution increases. Why?

Ans. Consider the example of an acidic buffer consisting of CH_3COOH and CH_3COONa.

CH_3COOH is a weak electrolyte and dissociated to a very little extent in water. When CH_3COONa (Salt), which is a strong electrolyte is added to CH_3COOH solution, the dissociation of CH_3COOH is suppressed due to common ion effect of CH_3COO^- ions

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$CH_3COONa_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

Since dissociation of CH_3COOH is suppressed, the conc of H_3O^+ ions in the solution decreases and the pH of the solution increases.

	$[CH_3COOH]$	$[CH_3COONa]$	pH
e.g.,	0.1 moldm^{-3}	0.00 moledm^{-3}	2.74
	0.1 moldm^{-3}	0.10 moledm^{-3}	4.74

Q. Describe the effect of common ion on solubility by giving examples.

Ans. The solubility of less soluble salts in water is suppressed by the addition of more soluble salts due to common ion effect. e.g.,

(i) The solubility of less soluble $KClO_3$ salt is decreased by the addition of KCl.

$$KClO_{3(s)} \rightleftharpoons K^+_{(aq)} + ClO_3^{-1}{}_{(aq)}$$

$$KCl_{(aq)} \rightleftharpoons K^{+1}_{(aq)} + Cl^{-1}_{(aq)}$$

(ii) The solubility of sparingly soluble $PbCrO_4$ is decreased by the addition of Na_2CrO_4

$$PbCrO_{4(s)} \rightleftharpoons Pb^{+2}_{(aq)} + CrO_4^{-1}{}_{(aq)}$$

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^{+1}_{(aq)} + CrO_4^{-1}{}_{(aq)}$$

Q. What will be the effect of change in pressure on NH_3 synthesis?

Ans. NH_3 gas can be prepared on industrial scale by Haber process. In the process N_2 and H_2 gases are reacted together to produce ammonia gas in a reversible reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92.46 kJ$$

In the reaction four moles of reactants produce two moles of product (NH_3). Therefore the reaction proceed with decrease in number of moles and decrease in volume. Now if we increase the pressure, the volume of reaction vessel will decrease. Due to decrease in volume, the equilibrium position shifts to towards right. Hence increase in pressure will move the reaction in forward direction and yield of NH_3 is increased.

Q. A catalyst does not affect the equilibrium constant comment on it?

Ans. A catalyst does not affect the equilibrium constant of a chemical reaction. A catalyst increases the rate of both forward and backward reactions and reduces the time to attain the state of equilibrium. The concentration of reactants and the products at equilibrium remain same.

As,

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Since concentrations of reactants and products are not affected, the equilibrium constant (K_c) remain constant.

Important Previous Board Questions

Q. Why is the manufacture of ammonia carried out at about 400°C when a lower temperature would favaour the formation of ammonia?

Q. How equilibrium constant "K_c" is used to predict the direction of reaction.

Q. How equilibrium constant, K_c explains the extent of reaction?

Q. When the concentration of salt is increased in an acidic buffer then the pH of the solution increases. Why?

Q. What is the effect of presence of common ion on solubility? Give example.

Q. In some reversible reactions direction of reaction is changed by change in pressure. Give reason.

Q. Why aqueous solution of salt derived from a very weak acid and a weak base may not be neutral?

Q. What is chemical equilibrium mixture?

For Answers study Scholar's CHEMISTRY (Objective) XI.

Chapter 9

SOLUTIONS

Phase

"Every sample of matter with uniform properties and a fixed composition is called a phase."

Examples

(i) Water at room temperature and normal pressure exist as a single liquid phase. It means that all the properties of water are uniform throughout the liquid phase.

(ii) Air, which is mainly composed of nitrogen and oxygen, exists as a gaseous phase.

SOLUTIONS

"A homogenous mixture of two or more kinds of different molecular or ionic substances is called a solution."

Binary solution

"A solution which consists of two components (solute and solvent) is called a Binary solution."

Example

Solution of sugar in water

Ternary solution

"A solution which consists of three components is called Ternary solution."

Example

The solution of salt, sugar and water is a ternary solution.

Solvent

"A substance which is present in a large quantity in a solution is called solvent."

Example

Water is a solvent in a sugar solution.

Solute

"A substance which is present in small quantity in a solution is called solute."

Example

Sugar is a solute in sugar solution.

Concentration of solution

"The amount of solute dissolved in a unit volume of solution (or a unit amount of solvent) is called concentration of solution."

Concentrated solution

"A solution containing relatively higher concentration of solute or low concentration of solvent is called concentrated solution."

Dilute solution

"A solution containing lower concentration of solute or higher concentration of solvent is called dilute solution."

CONCENTRATION UNITS OF SOLUTION

Percentage composition

The amounts of solute and solvent can be expressed in percentage composition by four different ways:

(a) Percentage Weight / Weight:

"It is the weight of a solute dissolved per 100 parts by weight of solution."

Example: 5% w/w sugar solution will contain 5 g of sugar dissolved in 100 g of solution in water. This solution contains 95 g of water.

Formula

$$\% \text{ by weight} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

(b) Percentage Weight / Volume

"It is the weight of solute dissolved per 100 parts by volume of solution."

Example: 10 g glucose dissolve in 100 cm^3 of solution is 10% w/v solution of glucose. The quantity of solvent is not exactly known

Note: In such solutions, the total volume of the solution is under consideration.

(c) Percentage Volume/Weight

"It is the number of cm^3 of a solute dissolved per 100 g of the solution."

Example: If we dissolve 10 cm^3 of alcohol in water and the total weight of solution is 100 g then it is 10% v/w solution of alcohol in water.

Note: In such type of solutions, we don't know the total volume of the solution.

(d) Percentage Volume/Volume

"It is the volume of solute dissolved by 100 cm^3 of solution."

This unit of concentration is best applicable to the solutions of liquids in liquids.

Example: 12% alcohol beverage is 12 cm^3 of alcohol per 100 cm^3 of solution.

Note: In such solutions, the total volume of the solution may not be necessarily equal to the sum of the volumes of solute and the solvent.

Molarity (M)

"The number of moles of solute dissolved per dm^3 of the solution is called molarity."

Unit

Its unit is mol dm^{-3}.

Formula

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in } dm^3}$$

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of solution in } dm^3}$$

Examples

(i) To prepare one molar solution of glucose in water, we take 180 g of glucose and add sufficient water to make the total volume 1 dm^3 (1litre) in a measuring flask.

(ii) In case of one molar solution of sucrose, 342 g of sucrose are dissolved in water to make it 1 dm^3.

Explanation

Since the volume of 342 g of sucrose is greater than 180 g of glucose so the volume of water in 1 molar sucrose is less than that of 1 molar glucose solution. Anyhow, to calculate the volume of the solvent, we need to know the density of the solute

Molarity refers to the concentration in mol dm^{-3}. Thus 2 mol dm^{-3} and 2 Molar (or 2M) mean the same: 2 moles of solute in 1 dm^3 of solution.

- Concentrations are sometimes referred in g dm^{-3}.
- Na_2CO_3 has a molar concentration of 0.100 mol dm^{-3} and a mass concentration of 10.6 g dm^{-3} of Na_2CO_3.

Important points

1. It is widely used in concentration unit of solution.
2. It is temperature dependent concentration unit of solution.

Molality (m)

"The number of moles of solute dissolved per 1 kg (1000 g) of solvent is called molality."

Units

Its unit is mol kg^{-1}.

Formula

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

Examples

(i) 180 g of glucose when dissolved in 1000 g of water gives one molal solution of glucose. The total mass of the solution is 1180 g. We don't know the volume of the solution. In order to know the volume we need the density of the solution.

(ii) For one molal sucrose solution, 342 g of sucrose are dissolved in 1000 g of H_2O.

Explanation

The molality of a solution is indirect expression of the ratio of the moles of the solute to the moles of the solvent. The molal aqueous solution of a solute say glucose or NaOH is dilute in comparison to its molar solution. The reason is that in molal solution the quantity of the solvent is comparatively greater.

Important point

- It is temperature independent concentration unit of solution.
- One molal solution of different solutes in water have their own masses and volumes.

Q5. What are the concentration units of solutions. Compare molar and molal solution?

Ans. **Concentration:** "The amount of solute dissolved in a unit volume of solution or a unit amount of solvent is called concentration."

Concentration Units: Various concentration units are used.Some are

(i) Percentage composition
(ii) Molarity
(iii) Molality
(iv) Mole fraction
(v) Parts per million

Comparison of molar and molal solutions

	Molar Solution	Molal Solution
1.	A solution which is prepared on the basis of molarity (mol dm^{-3}) is called molar solution.	A solution which is prepared on the basis of molality (mol kg^{-1}) is called molal solution.
2.	A molar solution is more concentrated than a relative molal solution as it contains same amount of solute in lesser amount of solvent.	A molal solution is dilute than a relative molar solution as same amount of solute is present in relatively larger amount of solvent.

3.	A volumetric flask is used to prepare molar solution	No volumetric flask is needed.
4.	As molarity is temperature dependent, therefore molar solution is effected by temperature	As molality is independent of temperature, therefore molal solutions are not effected by temperature.
5.	Example 60 g urea (1 mol) dissolved in one dm^3 of solution give rise to one molar (1 M) urea solution	Example: 60 g urea (1 mol) dissolved in one kg (1000 g) water give rise to one molal (1 m) urea solution.

Qs. (b) One has one molal NaCl solution and one molal glucose solution.

(i) Which solution has greater number of particles of solute.

Ans. One molal NaCl solution contains greater number of particles of solute as

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

NaCl being an electrolyte dissociates into ions. So in aqueous solution N_A (6.02×10^{23}) NaCl formula units give $2N_A$ (12.04×10^{23}) ions.

On the other hand glucose being a non-electrolyte solute is unable to ionize. Therefore one mole (6.02×10^{23}) glucose molecules give N_A molecules in aqueous solution.

(ii) Which solution has greater amount of solvent?

Ans. Both solution are one molal which mean that one mole of solute dissolved per one kilogram (1000 g) of water. So both solutions contain same amount of solvent.

(iii) How do we convert these concentrations into weight by weight percentage?

Given data: (i) One molal NaCl solution

(ii) One molal glucose solution.

It means

(i) 58.5 g mol^{-1} NaCl dissolved in 1000 g of water, so

mass of solute = 58.5 g

Mass of solution = 1000 g + 58.5 g = 1058.5 g

(ii) 180 g glucose dissolved in 1000 g H_2O, so

mass of solute = 180 g

mass of solution = 1000 g + 180 = 1180 g

Required: (i) w/w % NaCl solution = ?

(ii) w/w % glucose solution = ?

Solution:

Formula: $$w/w\,\% = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

(i) w/w % of NaCl $= \frac{58.5}{1058.5} \times 100 = 5.52\,\%$

(ii) w/w % of glucose $= \frac{180}{1180} \times 100 = 15.2\,\%$

Answers: (i) w/w % of one molal NaCl = 5.52 %

(ii) w/w % of one molal glucose = 15.2 %

Q6. (i) The concentration in terms of molality is independent of temperature but molarity depends upon temperature.

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

Since, the factor of mass is in denominator which is temperature independent, so molality does not change with change in temperature. On other hand,

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in } dm^3}$$

Volume is a temperature dependent factor. In case of molarity volume is present in denominator. So a change in temperature will change the volume and therefore molarity of the solution will also be changed Hence molarity depends upon temperature.

Q6. (vii) One molal solution of urea in water is dilute as compared to one molar urea solution. Although both contains same number of solute particles.

Ans. The concentration of two solutions having same amount of solute is decided on the basis of amount of solvent The solution containing more amount of solvent is dilute as compared to a solution containing lesser amount of solvent.

One molal solution of urea contains 60 g of urea dissolved per 1000 g of H_2O whereas one molar solution of urea contains 60 g urea dissolved per dm^3 of solution. Since amount of water is greater in one molal solution than in one molar solution of urea therefore one molal urea solution is dilute as compared to one molar solution.

Mole Fraction (x)

"The mole fraction of any component in a mixture is the ratio of number of moles of that component to the total number of moles of all the components present in the solution."

Important points

- There is no formal units of mole fraction.
- The sum of mole fraction of all the components of a solution must be equal to unity (1)
- It is temperature independent concentration unit of solution.
- This unit of concentration may be for any type of solution i.e. gas in gas, liquid in liquid or solid in liquid etc
- This unit is also applicable to a solution having more than two components.

Explanation

Let a solution has three components A, B and C. The number of moles are n_A, n_B and n_C respectively. If the mole fraction of A, B and C are denoted by x_A, x_B and x_C respectively then

$$x_A = \frac{n_A}{n_A + n_B + n_C}$$

$$x_B = \frac{n_B}{n_A + n_B + n_C}$$

$$x_C = \frac{n_C}{n_A + n_B + n_C}$$

$$x_A + x_B + x_C = 1$$

Mole percent

Mole percent = Mole fraction × 100

Q6. (ii) The sum of mole fractions of all the components in a solution is equal to unity.

Ans. **Mole fraction:** "The ratio of number of moles of a component to total number of moles of all All the components of the solution is called mole fraction of that component."

Considering a ternary solution containing three components A, B and C with 2, 3, and 5 moles

Number of moles respectively

$n_A = 2\ mol$

$n_B = 3\ mol$

$n_C = 5\ mol$

$n_T = n_A + n_B + n_C$

$n_t = 10\ mol$

$$\text{Mole fraction of component A} = x_A = \frac{n_A}{n_t} = \frac{2}{10} = 0.2$$

$$\text{Mole fraction of component B} = x_B = \frac{n_B}{n_t} = \frac{3}{10} = 0.3$$

$$\text{Mole fraction of component C} = x_C = \frac{n_C}{n_t} = \frac{5}{10} = 0.5$$

As the sum of mole fraction of all components of the solution is unity, so

$$x_A + x_B + x_C = 1$$

$$0.2 + 0.3 + 0.5 = 1$$

Hence it is proved that sum of mole fraction of all components of a solution is equal to unity.

Parts Per Million (ppm)

"The number of parts (by weight or volume) of a solute per million parts (by weight or volume) of the solution is called ppm."

This unit is used for very low concentration of solution.

Examples

- To express the impurities of substances in water.
- To express the concentration of pollutants in air.
- To express the concentration of chlorine in public supply of potable water.

Formula

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Interconversion of Various Concentration Units of Solutions

Sometimes, we get prepared solutions from the chemical supply houses. For example, we are working with a solution whose molarity is given by the supplier, but we need to know its molality or w/w percentage. For such purpose, we need to convert one unit of concentration into other. These conversions are usually done if we know the formula masses and the densities of the solutes or solutions. Following table shows the five important chemicals whose w/w%, molarities and densities are given. One should be able to interconvert these concentration units into each other and moreover to molalities and mole fractions for laboratory work.

Name of Acid	% (w/w)	Molarity ($M\ dm^{-3}$)	Density (gcm^{-3})
H_2SO_4	98 %	18	1.84
H_3PO_4	85.5 %	4.8	1.70
HNO_3	70.4 %	15.9	1.42
HCl	37.2 %	12.1	1.19
CH_3COOH	99.8 %	17.4	1.05

Example (6):

Calculate the molality of 8% w/w NaCl solution.

Ans. **Given Data:**

w/w percentage of solution = 8%

Required:

Molality (m) = ?

Solution:

Molality is the number of moles of solute per kg of solvent.

8% w/w NaCl solution means that 8gm of NaCl are dissolved in 100g of solution.

So mass of water in solution = 100 – 8 = 92g

$$\text{Number of moles of NaCl} = \frac{8g}{58.5g\ mol^{-1}} = 0.1367\text{mole}$$

$$\text{Mass of water in kg} = \frac{92g}{1000} = 0.092kg$$

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$= \frac{0.1367\text{moles}}{0.092kg} = 1.487\ \text{moles}\ kg^{-1}$$

$$\text{Molality} = 1.487\ \text{moles}\ kg^{-1}$$

Example (7):

Hydrochloric acid available in laboratory is 36% (w/w). The density of HCl solution is $1.19gcm^{-3}$. Determine the molarity of HCl solution.

Ans. **Given Data:**

Hydrochloric acid = 36% (w/w)

Density of HCl solution = $1.19gcm^{-3}$

Required:

Molarity of HCl solution = ?

Solution:

36% (w/w) HCl solution means that 36g of HCl dissolved in 100g of solution.

Mass of HCl = 36g

Mass of solution = 100g

In case of molarity, the final volume of solution is $1000cm^3$. Convert this volume into mass

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Mass} = \text{Density} \times \text{Volume}$$

$$= 1.19 \times 1000 = 1190g$$

100g of solution has HCl = 36g

$$1g \text{ of solution has HCl} = \frac{36}{100}$$

$$1190g \text{ of solution has HCl} = \frac{36}{100} \times 1190$$

$= 428.4g$

Molar mass of HCl = 36.5g/mole

Number of moles of HCl, in 428.4g of HCl $= \frac{428.4}{36.5}$

$= 11.73$

Molarity of HCl = 11.73 moles dm^{-3}

Example (8):

9.2 molar $HClO_4$ is available from market. The density of this solution is 1.54gcm^{-3}. What is the percentage by weight of $HClO_4$.

Given Data:

Molarity of $HClO_4$ = 9.2g mole dm^{-3}

Density of Solution = 1.54gcm^{-3}

Required:

Percentage by weight of $HClO_4$ = ?

Solution:

Let us calculate the mass of solution, which is 1dm^3 in volume and has 9.2 moles of $HClO_4$ in it.

Mass = Volume × Density

Mass of 1000cm^3 solution = 1000cm^3 × 1.54gdm^{-3}

= 1540g

Molar mass of $HClO_4$ = 1 + 35.5 + 16 × 4 = 100.5g mol^{-1}

To convert 9.2 moles of $HClO_4$ into mass

$$\text{Mole} = \frac{\text{Mass}}{\text{Molar Mass}}$$

Mass = Mole × Molar Mass = 9.2 mole × 100.5gmole^{-1}

= 924.6g

Mass of water (H_2O) = Mass of solution – Mass of $HClO_4$

= 1540 – 924.6 = 615.4g

$$\% \text{ of } HClO_4 \text{ by weight} = \frac{\text{Mass of } HClO_4}{\text{Mass of solution}} \times 100$$

$$= \frac{924.6}{1540} \times 100$$

$$= 60.013$$

% of H_2O by weight = 100 – Mass of $HClO_4$

= 100 – 60.013 = 39.99

% of $HClO_4$ by weight = **60.013%**

Q6. (iii) 100 g of 98 % H_2SO_4 has a volume 54.34 cm^3 of H_2SO_4 (density = 1.84 g cm^{-3})

Ans. Given:

Mass of 98% H_2SO_4 solution	= 100 g
Volume of solution	= 54.34 cm^3
Density	= 1.84 g cm^{-3}

Prove:

Mass per unit volume is known as density.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

$$V = \frac{m}{d} = \frac{100\text{ g}}{1.84\text{ g cm}^{-3}} = 54.34\text{ cm}^3$$

So it is calculated that 100 g 98 % H_2SO_4 has a volume of 54.34 cm^3 of H_2SO_4.

Types of Solutions

There are nine possible types of solutions:

Common Types and Examples of Solutions

State of Solute	State of Solvent	Examples
Gas	Gas	Air
Gas	Liquid	O_2 in water, CO_2 in water
Gas	Solid	H_2 adsorbed by palladium
Liquid	Gas	Mist, fog, clouds, liquid air pollutants
Liquid	Liquid	Alcohol in water, milk, benzene in toluene
Liquid	Solid	Mercury in silver, butter, cheese
Solid	Liquid	Sugar in water, jellies, paints
Solid	Gas	Dust particles in smoke
Solid	Solid	Metal alloys pearls, opals, carbon in iron (steel)

Solutions of Solids in Liquids

When a solid comes in contact with a suitable liquid, it dissolves forming a solution i.e a homogeneous mixture This process of dissolution can be explained in terms of attraction between the particles of a solute and that of a solvent The molecules or ions in solids are arranged in such a regular pattern that the intermolecular or inter ionic forces are at a maximum. The process of dissolution is to overcome these forces of attraction holding together the solute molecules or ions in the crystal lattice by the solute-solvent forces.

In molecular crystals

In molecular crystals, the intermolecular forces of attraction are either dipole-dipole or London dispersion type These forces are relatively weak and can easily be overcome. Hence, non-polar or less polar molecular crystals usually dissolve in non-polar solvents like benzene.

In crystal lattice

In crystal lattice, the inter-molecular or inter-ionic forces of attraction between highly polar molecules or ions are quite strong hence the polar solids fail to dissolve non-polar solvents. These strong electrostatic forces cannot be overcome or shattered by the weak solute-solvent attractions.

Example of cane sugar

Due to hydrogen bonding, it has tightly bound molecules, so it will not be dissolved by solvents like kerosene oil, petrol, benzene etc. It will be dissolved readily in water because water attracts sugar molecules almost in the same way as the sugar molecules attract one another.

In ionic solids

The inter-ionic forces of attraction are very strong in ionic solids, so equally strong polar solvents are needed to dissolve them. Such solids cannot be dissolved by moderately polar solvents. e.g. Acetone, a moderately polar solvent fails to dissolve sodium chloride, which is an ionic solid.

Principle

Thus, the solubility principle is, **"Like dissolves Like."**

Solutions of Liquids in Liquids

The solutions of liquids in liquids may be divided into three classes.

(i) Completely Miscible Liquids

The liquids which dissolve in each other in all proportions are called completely miscible liquids.

Examples

- Water and ethanol.
- Ethanol and ether.

Important points

- The properties of such solutions are not strictly additive.
- Generally, the volume decreases on mixing (if the new forces formed are stronger) but in some cases it increases.
- Heat may be evolved or absorbed during the formation of such solutions.
- These types of solutions can usually be separated by fractional distillation.

(ii) Partially Miscible Liquids

Those liquids which dissolve into each other up to a limited extent are called the partially miscible liquids. Water and ether ($C_2H_5—O—C_2H_5$) are partially miscible liquids. Ether dissolves water to the extent of about 1.2%. Water dissolves ether up to the extent of 6.5%.

Explanation

As the mutual solubilities are limited, the liquids are only partially miscible. On shaking, equal volumes of water and ether two layers are formed. Each liquid layer is a saturated solution of the other liquid. Such solutions are the conjugate solutions.

Conjugate solutions

"Those solutions or liquids layers which are the saturated solution of each other are called conjugate solutions."

Factor

The mutual solubility of these conjugate solutions is affected by temperature changes.

Examples

(a) Phenol water system.

(b) Tri-ethylamine-water system.

(c) Nicotine-water system.

Q9 (b) Explain the effect of temperature on phenol-water system.

Phenol-Water System

If equal volumes of water and phenol are mixed together, they show partial miscibility.

At room temperature

It has been observed that around room temperature, phenol will dissolve in a lot of water giving us the upper layer and water will dissolve in a lot of phenol giving us the lower layer. At 25°C, the upper layer is 5% solution of phenol in water and the lower layer is 30% water in phenol. These two solutions are conjugate solutions to each other. The lower layer has a greater density due to greater percentage of phenol. Water acts as a solute in the lower layer while phenol is a solute in the upper layer.

At increased temperature

When the temperature of water-phenol system is increased, the compositions of both layers change. Water starts travelling from upper to lower layer and phenol travels from lower to upper layer. When the temperature of this system approaches 65.9°C, a homogeneous mixture of two components is obtained. This homogeneous mixture contains 34% phenol and 66% water. This temperature of 65.9 °C is called critical solution temperature of water – phenol system.

Critical Solution Temperature / Upper Consulate Temperature

"The temperature at which two conjugate solutions merge into one another to form homogeneous solution is called upper consulate temperature or critical solution temperature."

Examples

- Water-aniline system has a single layer at 167.0°C with 15% water.
- Methanol cyclohexane system has upper consulate temperature of 49.1°C with 29% methanol.

(iii) Practically Immiscible Liquids

Those liquids which do not dissolve into each other in any proportion are immiscible.

Examples: **(i)** Water and benzene ($H_2O + C_6H_6$) **(ii)** Water and carbon disulphide ($H_2O + CS_2$)

Ideal and Non-Ideal Solutions

When two or more than two liquid substances are mixed, the solutions may be ideal or non-ideal. To distinguish between such solutions we look at the following aspects:

(i) If the forces of interactions between the molecules of different components are same as when they were in the pure state, they are ideal solutions, otherwise non-ideal.

(ii) If the volume of solution is not equal to the sum of the individual volumes of the components, the solution is non-ideal.

(iii) Ideal solutions have zero enthalpy change as their heat of solution.

(iv) If the solutions obey Raoult's law, then they are ideal. This is one of the best criterion for checking the ideality of a solution.

Q7. What are non ideal solutions? Discuss their types and give three example of each.

Comparison between Ideal and Non-Ideal Solutions

Ideal solutions	Non-Ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
1. Obey Raoult's law at every range of concentration.	Do not obey Raoult's law.	Do not obey Raoult's law.
2. $\Delta H_{mix} = 0$; neither heat is evolved nor absorbed during dissolution.	$\Delta H_{mix} > 0$. Endothermic dissolution; heat is absorbed.	$\Delta H_{mix} < 0$. Exothermic dissolution, heat is evolved.
3. $\Delta V_{mix} = 0$; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{mix} > 0$. Volume is increased after dissolution.	$\Delta V_{mix} < 0$ Volume is decreased during dissolution
4. $P = p_A + p_B = p^\circ_A X_A + p^\circ_B X_B$ i.e., $p_A = p^\circ_A X_A$; $p_B = p^\circ_B X_B$	$\therefore p_A + p_B > p^\circ_A X_A + p^\circ_B X_B$ $p_A > p^\circ_A X_A$; $p_B > p^\circ_B X_B$	$p_A + p_B < p^\circ_A X_A + p^\circ_B X_B$ $p_A < p^\circ_A X_A$, $p_B < p^\circ_B X_B$
5. $A - A, A - B, B - B$ interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character	A-B attractive force should be weaker than A-A and B-B attractive forces. 'A' and 'B' have different shape, size and character.	A-B attractive force should be greater than A-A and B-B attractive forces 'A' and 'B' have different shape, size and character.
6. Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing higher vapour pressure than the expected value	Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally

Examples: Dilute solutions; Benzene+toluene; n-hexane+n-heptane; chlorobenzene + bromobenzene; ethyl bromide + ethyl iodide; n-butyl chloride + n-butyl bromide.	**Examples:** acetone + ethanol; acetone + CS_2 water + methanol; water + ethanol; CCl_4 + toluene; $CCl_4 + CHCl_3$; acetone + benzene; $CCl_4 + CH_3OH$; Cyclohexane + ethanol.	**Examples:** acetone + aniline; acetone + chloroform; $CH_3OH + CH_3COOH$; $H_2O + HNO_3$; chloroform + diethyl ether; water + HCl; acetic acid + pyridine: chloroform + benzene.

Q13. What is Raoult's law? Give its three statements. How this law can help us to understand the ideality of a solution.

RAOULT'S LAW

Raoult's law can be defined in three ways:

Statement 1

"The vapour pressure of a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in solution."

Mathematical form

$$p = p^{\circ}x_1 \qquad \ldots(i)$$

Where,

p = Vapour pressure of solvent in the solution
p° = Vapour pressure of pure solvent
x_1 = Mole fraction of solvent

Statement 2

"The lowering of vapour pressure is directly proportional to the mole fraction of solute."

Mathematical form

From eq. (i)

$$p = p^{\circ}x_1$$

We know that,

$$x_1 + x_2 = 1$$

or

$$x_1 = 1 - x_2$$

Putting the value

$$p = p^{\circ}(1 - x_2)$$
$$p = p^{\circ} - p^{\circ}x_2$$
$$p^{\circ} - p = p^{\circ}x_2$$
$$\Delta p = p^{\circ}x_2 \qquad \ldots(ii)$$

Where,

Δp = lowering of vapour pressure
x_2 = mole fraction of solute

Statement 3

"The relative lowering of vapour pressure is equal to the mole fraction of solute."

Mathematical form

From eq. (ii)

$$\Delta p = p^{\circ}x_2$$
$$\frac{\Delta p}{p^{\circ}} = x_2 \qquad \ldots(iii)$$

Factors

The relative lowering of vapour pressure
(i) is independent of the temperature.
(ii) depends upon the concentration of solute.
(iii) is constant when equimolecular proportions of different solutes are dissolved in the same mass of same solvent.

Q6. (iv) Relative lowering of vapour pressure is independent of temperature.

Ans. According to one of the statements of Raoult's law "The relative lowering of vapour pressure is equal to the mole fraction of solute."

$$\frac{\Delta p}{p^{\circ}} = x_2$$

While mole fraction of solute means "The ratio of number of moles of the solute to total number of moles of the solution."

$$x_2 = \frac{n_2}{n_1 + n_2}$$

Mole is an expression of atomic mass, molecular mass, formula mass or ionic mass of a substance in grams. As mass is independent of temperature therefore mole, mole fraction and ultimately relative lowering of vapour pressure $\frac{\Delta p}{p^{\circ}}$ is also a temperature independent element.

RAOULT'S LAW (when both components are volatile)

Raoult's law can be applied to understand the relationship between mole fractions of two volatile components and their vapour pressures before making the solution and after making the solution.

Consider two liquids A and B with pressures p_A° and p_B° in the pure state at given temperature

After making the solution, the vapour pressure of both liquids are changed. Let the vapour pressure of these liquids in the solution state be p_A and p_B with their mole fractions x_A and x_B respectively.

Applying Raoult's law to both components.

$$p_A = p_A^{\circ}x_A$$
$$p_B = p_B^{\circ}x_B$$
$$P_t = p_A + p_B$$
$$= p_A^{\circ}x_A + p_B^{\circ}x_B \text{ (where } P_t \text{ is total vapour pressure)}$$

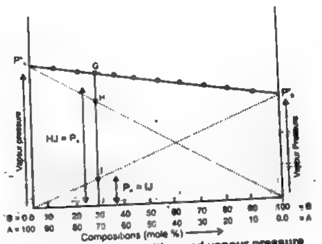
Since

$$x_A + x_B = 1$$
$$x_B = 1 - x_A$$
$$P_t = p_A^{\circ}x_A + p_B^{\circ}(1 - x_A)$$
$$P_t = p_A^{\circ}x_A + p_B^{\circ} - p_B^{\circ}x_A$$
$$P_t = (p_A^{\circ} - p_B^{\circ})x_A + p_B^{\circ} \ldots\ldots\ldots\ldots\ldots (i)$$

The component A is low boiling liquid and B is high boiling liquid. The vapour pressure of A is more than B at a given temperature. The equation (i) is a straight line equation.

Graphical explanation

If a graph is plotted between x_B or mole % of B on x-axis and P_t on y-axis, a straight line will be obtained.



Graph between composition and vapour pressure

Only those pairs of liquids give straight lines which form ideal solutions. So, Raoult's law is one of the best criterion to judge whether a solution is ideal or not.

All the possible solutions of two components A and B have their vapours pressures on the straight line connecting p°_A with p°_B. All such solutions will be ideal. Each point on this line represents the vapour pressure of solution at a given temperature.

The two dotted lines represent the partial pressures of individual component of solution. They show the increase of vapour pressure of a component with increase in its mole fraction in solution.

In order to explain it, consider a point G on the straight line. This point represents the vapour pressure of solution with 30% moles contribution of the component B and 70% moles contribution of component of A. Since A is more volatile, so its contribution towards the vapour pressure of solution is represented by p_A. The contribution of the less volatile component B is represented by p_B. Similarly, we can calculate the relative contributions of A and B towards the total vapour pressure by taking their points along the line joining p°_A to p°_B.

Conclusion

The total vapour pressure of the solution (P_t) corresponding to the point G will be equal to the sum of the vapour pressures of the individual components ($p_A + p_B$) as shown in the figure.

Q6. (viii) Non-ideal solutions do not obey the Raoult's law:

Ans. In non-ideal solutions, the solute-solute interactions and solvent-solvent interaction are not equal to solute-solvent interaction. These forces or interactions are either greater or lesser than that of pure components. Therefore the volume and enthalpy of solution are not equal to sum of volumes and enthalpy of components i.e.,

$$V \neq V_1 + V_2 \quad \text{or} \quad \Delta V \neq 0$$

$$H \neq H_1 + H_2 \quad \text{or} \quad \Delta H \neq 0$$

Therefore non ideal solutions do not obey Raoult's law. Hence they are called non-ideal solutions.

Vapour Pressures of Liquid-Liquid Solutions

Binary mixtures of miscible liquids may be classified as:

(i) Ideal solutions
(ii) Non-ideal solutions

The vapour pressures of solutions provide a simple picture about their behaviour.

Ideal solutions

"Those solutions, which obey Raoult's law are called ideal solutions."

In ideal solution:

(i) The forces of interactions between the molecules of different components are same as when they are in the pure state.
(ii) The volume of the solution is equal to the sum of individual volumes of the components i.e., $\Delta V = 0$
(iii) They have zero enthalpy change as their heat of solution i.e., $\Delta H = 0$

Examples: Some typical ideal solutions forming liquid pairs are: chlorobenzene-bromobenzene, ethyl iodide-ethyl bromide, benzene-ether, benzene-toluene etc.

Generally, those liquid compounds, which have similar structure and polarity form ideal solutions.

Q8. (a) Explain fractional distillation. Justify the two curves when composition is plotted against boiling point of solutions.

Fractional Distillation of Ideal Mixture of Two Liquids

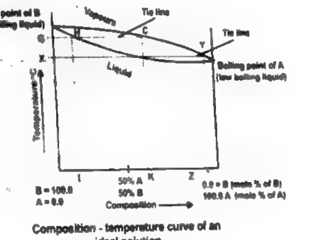
Fractional distillation

"A type of distillation in which the components of a mixture are separated on the basis of difference in their boiling points is called fractional distillation."

Composition-temperature graph

Let us have two liquids A and B, which form a completely miscible solution. A is a more volatile component so its boiling point is less than B. If we have various solutions of these two components and a graph is plotted between composition on x-axis and temperature on y-axis, then two curves are obtained.

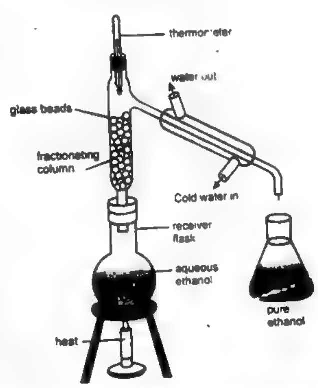
- The upper curve represents the composition of the vapours of different solutions.
- The lower curve represents the composition of the liquid mixtures.



Composition - temperature curve of an ideal solution

The reason is that at any temperature, the composition of vapours is different from the composition of liquid mixture.

Consider the temperature, corresponding to the point G. It is the boiling point of solution corresponding to composition I. It meets liquid curve at point H and the vapour curve at the point C. The composition of liquid mixture corresponding to the point H is shown by the point I. At the point I, the mixture has greater percentage of B and less percentage of A. While at the same temperature, the vapours of the mixture have the composition K. At point K, the percentage of A is comparatively greater than B when we compare it with composition of liquid mixture corresponding to point I. Because A is a low boiling liquid, it is present in the vapour state in greater percentage than at point I.



If the temperature of the mixture is maintained corresponding to point G, the distillate will have greater percentage of A and residue will have greater percentage of B. The reason is that the fraction going to distillate is that which is in vapour state and it has greater percentage of A. The distillate of composition K is again subjected to distillation. Its boiling point is X, and at this temperature the distillate of composition Z is obtained. This distillate of composition Z is further distilled. In this way, the distillate becomes more and more rich in A and residue is more and more rich in B. So, process of distillation is repeated again and again to get the pure component A. Thus we can completely separate the components by fractional distillation.

Zeotropes

Those solutions, which can be distilled with the change in their composition, are called zeotropes or zerotropic mixtures.

Example

Mixture of water and methanol is a zeotrope which can be separated by fractional distillation.

Non-ideal solutions

Many solutions do not behave ideally. They show deviations from Raoult's law due to differences in their molecular structures i.e. size, shape and intermolecular forces. Formation of such solutions is accompanied by changes in volume and enthalpy. The vapour pressure deviations may be positive or negative in such solutions.

The deviations of non-ideal solutions from Raoult's law are of two types.

(a) Positive deviations

(b) Negative deviations

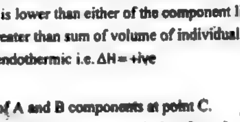
Q.6 (vi) The total volume of the solution by mixing 100 cm^3 of water with 100 cm^3 of ethylalcohol may not be equal to 200 cm^3. Justify it.

Ans. Water is a polar angular molecule having hydrogen bonding between its molecules.

Similarly ethyl alcohol also shows hydrogen bonding due to presence of –OH group.

When both the liquids are mixed the volume of solution is slightly greater than sum of individual volumes of both components due to two reasons.

(i) hydrogen-bonding between water and ethyl alcohol molecules is comparatively weaker than individual components.



(ii) Due to bent structure of both molecules, during mixing the molecules entangle with each other leaving some spaces between them.

Mathematically we can say that volume of solution is greater than sum of the volume of water and volume of ethyl alcohol. This shows that this mixture deviate from Raoult's Law.

(a) Positive Deviations

If a graph is plotted between composition and vapour pressure of a solution which shows positive deviation from Raoult's law, the total vapour pressure curve rises to a maximum.

In these solutions:

(i) The vapour pressure of some of solutions are above the vapour pressure of either of the pure components.

(ii) The boiling point of the mixture is lower than either of the component liquids.

(iii) The volume of the solution is greater than sum of volume of individual components.

(iv) Formation of these solutions is endothermic i.e. $\Delta H = +ive$

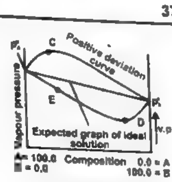
Graphical explanation

Let us consider the mixture of A and B components at point C.

At point C, the mixture has the highest vapour pressure and ,therefore, the lowest boiling point. On distilling this type of solution, the first fraction will be a constant boiling point mixture i.e. azeotropic mixture having a fixed composition corresponding to the maximum point. For this type of solution, it is not possible to bring about complete separation of components by fractional distillation.

Example

Ethanol-water mixture is an example of this type. It boils at 78.1°C with 4.5% water and 95.5% alcohol. 78.1°C is lower than the boiling point of ethanol (78.5°C) and water (100°C).



Non-ideal solutions and azeotropic mixtures

(b) Negative Deviations

If a graph is plotted between composition and vapour pressure of a solution which shows negative deviation from Raoult's law, the total vapour pressure curve rises to a minimum.

In these solutions:

(i) The vapour pressure of some of solutions are below the vapour pressure of either of the pure components

(ii) The boiling point of the mixture is higher than either of the component liquids.

(iii) The volume of the solution is lesser than sum of volume of individual components.

(iv) Formation of these solutions is exothermic i.e. $\Delta H = -ive$

Graphical explanation

Let us consider a point E in the graph. Here, the more volatile component A is in excess. On distilling this solution, the vapours will contain more of A and the remaining mixture becomes richer in less volatile component B. Finally, we reach the point D where vapour pressure is minimum and the boiling point is maximum. At this point, the mixture will distill unchanged in composition. Therefore, it is not possible to separate this type of solution completely into its components.

Example

Hydrochloric acid solution in water is an example of such kind of solutions. HCl forms an azeotropic mixture with water, boiling at 110°C and containing 20.24% of the acid.

Q.(a) What are azeotropic mixtures? Explain them with the help of graphs?

Azeotropic Mixture

"Those mixtures which boil at constant temperature and distill over without change in composition at any temperature like a pure chemical compound are called azeotropic mixtures or azeotropes."

Examples

- Mixture of water and ethanol (ethanol 95.5% and water 4.5%).
- Mixture of water and HCl (HCl 20.24% and water 79.76%).

Important points

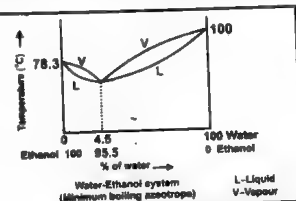
(i) Azeotropic mixtures cannot be distilled by fractional distillation because they have same composition in distillate as well as in residue.

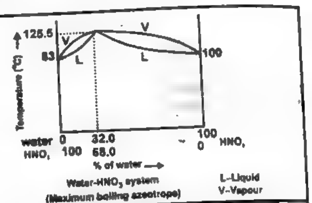
(ii) These mixtures cannot be regarded as chemical compound as changing the total pressure along with boiling point changes their composition. Whereas, for a chemical compound the composition remains constant over a range of temperature and pressure.

Types of azeotropic mixtures

Azeotropic mixtures are of following two types:

Minimum boiling point azeotropes	Maximum boiling point azeotropes
Minimum boiling point azeotropes are obtained from solutions showing positive deviation.	Maximum boiling point azeotropes are obtained from solutions showing negative deviation.
Boiling point of such solutions is less than their components.	Boiling point of such mixtures is greater than their components.





Mixture	% Composition of azeotrope	BP (°C)
Water-Ethanol	95.5 Ethanol	78.5°C
Pyridine-Water	57.00 Pyridine	92.60°C
Ethanol-Benzene	32.40 Ethanol	67.80°C
Acetic acid-Tolune	28.00 Acetic acid	105.40°C

Mixture	% Composition of azeotrope	BP (°C)
$HNO_3 - H_2O$	68% Nitric acid	125.5°C
CH_3COOH - Pyridine	65% Pyridine	139.0°C
$CHCl_3$-Acetone	80% Chloroform	65.0°C
HCl - Water	79.76% Water	110°C

Q8. (b) The solutions showing positive and negative deviation cannot be fractionally distilled at their specific compositions. Why?

Ans. A solution (zeotropic mixture) can only be fractionally distilled when the compositions of liquid and vapour phases are different.

A fraction is distilled over again and again to get more volatile component in the distillate and less volatile in residue of fractional distillation.

Non-ideal solutions showing positive or negative deviation from Raoult's law, cannot be fractionally distilled at a specific composition because the composition of liquid and vapour phase of that solution is same.

Whenever distillation is performed a mixture of fixed composition is obtained called **azeotropic** mixture as a distillate or residue. For example, 95.5% ethanol solution in H_2O is an azeotropic mixture showing positive deviation.

Solubility

"The concentration of the solute in the solution when it is in equilibrium with solid substance at a particular temperature is called solubility."

or

"The amount of solute dissolved in a solvent to give a saturated solution at a particular temperature is called solubility."

Representation

Solubility is expressed in terms of number of grams of solute in 100 g of solvent.

Examples

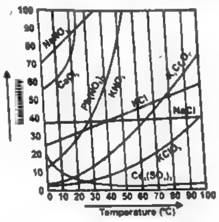
- Saturated solution of NaCl in water at 0°C contains 37.5 g of NaCl in 100 g of water.
- The solubility of $CuSO_4$ in water at 100°C is 75.4 g per 100 g of water and at 0°C is 14.3g/100g of water.

Determination of solubility

To determine the solubility of a substance, a saturated solution of a solid is prepared at a constant temperature. Then this solution is filtered. A known volume of this solution is evaporated in a china dish and from the mass of the residue, the solubility can be calculated.

Solubility curves

"A graphical representation between temperature and solubility of the solution is called solubility curve."



Continuous solubility curves

Types of solubility curves

Solubility curves are of following two types:

(a) Continuous solubility curves

(b) Discontinuous solubility curves

Continuous solubility curve

These curves don't show sharp breaks anywhere. These include

(i) Straight line ⟶ NaCl, KCl, $NaNO_3$

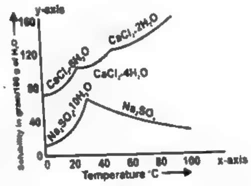
(ii) Abrupt curve ⟶ $KClO_3$, $K_2Cr_2O_7$, KNO_3, $Pb(NO_3)_2$

(iii) Decline curve ⟶ $Ce_2(SO_4)_3$, Li_2CO_3

$Ce_2(SO_4)_3$ shows the exceptional behaviour whose solubility decreases with the increase in temperature and becomes constant from 40°C onwards. Anyhow, it shows continuous solubility curve.

Discontinuous solubility curves

Sometimes, the solubility curves show sudden changes of Solubilities and these curves are called discontinuous solubility curves. e.g. $Na_2SO_4.10H_2O$, $CaCl_2.6H_2O$ etc.



Discontinuous solubility curves

Actually, these curves are combination of two or more solubility curves. At the break, a new solid phase appears and another solubility curve of that new phase begins. It is the number of molecules of water crystallization which changes and hence solubility changes.

Fractional Crystallisation

It is observed that the variation in solubility with temperature is different for different substances. For example, the change in solubility in case of KNO_3, is very rapid with changing temperature, while such a change is more gradual in other cases like KBr, KCl, alanine, etc. These differences in the behaviuor of compounds provide the basis for fractional crystallization, which is a technique for the separation of impurities from the chemical products.

By using the method, the impure solute is dissolved in a hot solvent in which the desired solute is less soluble than impurities. As the hot solution is cooled, the desired solute being comparatively less soluble, separates out first from the mixture, leaving impurities behind. In this way, pure desired product crystallizes out from the solution.

Q10. (a) What are colligative properties? Why are they called so?

COLLIGATIVE PROPERTIES OF SOLUTIONS

"Those properties of a solution which depend upon the number of solute and solvent molecules or ions and are independent of the nature of the solute are called colligative properties."

The word colligative is derived from a Greek word, "Collegatus" meaning "collected together."

Colligative properties of a dilute solution

Following are the colligative properties of a dilute solution.

(i) Lowering of vapour pressure.

(ii) Elevation of boiling point.

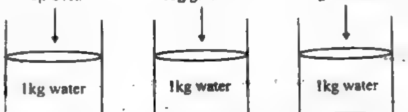
(iii) Depression of freezing point.

(iv) Osmotic pressure.

The practical applications of colligative properties are numerous. The study of colligative properties has provided us with methods of molecular mass determination and has also contributed to the development of solution theory.

Why some of the properties are called colligative

The reason for these properties to be called colligative can be explained by considering three solutions.



Let us take 6 g of urea, 18 g of glucose and 34.2 g of sucrose and dissolve them separately in 1 kg of H_2O. This will produce 0.1 molal solution of each substance. Pure H_2O has certain value of vapour pressure at a given temperature. In these three solutions, the vapour pressures will be lowered. The reason is that the molecules of a solute present upon the surface of a solution decrease the evaporating capability.

Variation in the vapour pressure

Apparently, it seems that sucrose solution should show the maximum lowering of vapour pressure while urea should have the minimum lowering of vapour pressure. The reality is that the lowering of vapour pressure in all these solutions will be same at a given temperature. Actually, the number of particles of the solute in all the solutions are equal. We have added 1/10th of Avogadro's number of particles (6.02×10^{22}). The lowering of vapour pressure depends upon the number of solute particles and not upon their molar mass and structures. Well, it should be kept in mind that these three solutes are non-volatile and non-electrolyte.

Variation in boiling points and freezing points

The boiling points of these solutions are higher than that of pure solvent. It is observed that the boiling point elevation of these three solutions is 0.052°C. Similarly, freezing points will be depressed for these solutions and the value of depression in these three cases is 0.186°C. The reason again is that the elevation of boiling point and the depression of freezing point depend upon number of particles of solute.

For one molal solution

Now, let us deduce the values of elevation of the boiling point and the depression of the freezing point of water for 1 molal solutions. For that purpose, try to dissolve 60 g of urea, 180 g of glucose and 342 g of sugar separately in 1kg of water. The elevation of boiling point and depression of freezing point of water will be 0.52°C and 1.86°C, respectively. All the three solutions will boil at 100.52°C and freeze at −1.86°C. These values of elevation of boiling point and depression of freezing point are called molal boiling point constants and molal freezing point constants of H_2O denoted by K_b and K_f respectively.

Molal boiling point constant (ebullioscopic constant)

"The elevation in boiling point of a liquid, when one mole of a non–volatile, non-electrolyte solute is dissolved in one kilogram of a solvent is called molal boiling point constant or Ebullioscopic constant."

- It is denoted by K_b

Molal Freezing point constant (cryoscopic constant)

"The depression in the freezing point of a liquid, when one mole of a non–volatile, non-electrolyte solute is dissolve in one kilogram of a solvent is called molal freezing point constant or Cryoscopic constant."

- It is denoted by K_f
- These constants depend upon the nature of solvent and not upon the nature of solute.

K_b and K_f values for some solvents

Solvent	B.P (°C)	K_b (°C/m)	F.P(°C)	K_f (°C/m)
H_2O	100	0.52	0	1.86
Ether	34.4	2.16	-116.3	1.79
Acetic acid	118	3.07	17	3.90
Ethanol	79	1.75	-114.5	1.99
Benzene	80	2.70	5.5	5.10

Conditions to study colligative properties

To observe the colligative properties, following conditions should be fulfilled by the solutions.

(i) Solution should be dilute

(ii) Solute should be non-volatile

(iii) Solute should be non-electrolyte

Q. (v) Colligative properties are obeyed when the solute is non-electrolyte and also when the solutions are dilute?

Ans. "The colligative properties are the properties of the solution that depend only on the number of solute and solvent molecules or ions."

With the change in number of particles, the colligative properties change.

In case of electrolyte, the number of particles of solute increases in solution due to ionization of electrolyte, hence the colligative properties change. For example, 1 molal urea solution, 1 molal NaCl solution and one molal $MgCl_2$ solution, all have different colligative properties due to different number of solute particles. Hence a solute should be non-electrolyte to study colligative properties.

In case of concentrated solution, solute particles form clusters so the tendency of solvent to evaporate is also effected. Therefore only dilute solutions are used to study colligative properties.

Q10. (b) What is the physical significance of K_b and K_f.

Ans. **Molal boiling point constant (K_b):** The elevation of boiling point of the solution when one mole of non-volatile and non-electrolyte solute is dissolved in one kg of solvent is called molal boiling point constant or ebullioscopic constant.

Molal freezing point constant (K_f): The depression in freezing point of solution when one mole of non-electrolyte and non-volatile solute is dissolved in one kg of solvent is called molal depression in freezing point or cryoscopic constant.

Unit: Both are expressed in °C/m. Their values depend upon nature of solvent

Significance: By knowing these values, one can guess the change in colligative properties due to different concentration of solute or using an electrolyte solute.

e.g., K_b for water is 0.52 °C/m

K_f for water is 1.86 °C/m

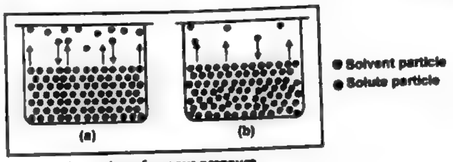
Q11. How do you explain that the lowering of vapour pressure is a colligative property?

How do we measure the molar mass of a non-volatile, non-electrolyte solute in a volatile solvent?

Lowering of Vapour Pressure

In a pure liquid, the particles can escape from all over the surface of liquid. But when a non-volatile solute is dissolved in a solvent, the escaping tendency of solvent particles from the surface of the solution decreases and its vapour pressure is lowered.

A quantitative relationship between the change of vapour pressure of a solvent due to addition of non-volatile and non-electrolyte solute and the mole fraction of solute has been given by Raoult



Lowering of vapour pressure

According to Raoult's law

"The relative lowering of vapour pressure is equal to the mole fraction of solute."

$$\frac{\Delta p}{p^\circ} = x_2$$

Where, x_2 is the mole fraction of the solute

If n_2 and n_1 are the number of moles of a solute and solvent respectively, then,

$$x_2 = \frac{n_2}{n_1 + n_2}$$

So,
$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1 + n_2}$$

For a dilute solution, n_2 can be ignored in denominator,

Hence,
$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1}$$

The number of moles of solute and solvent are obtained by dividing their masses in grams with their respective relative molecular masses.

If W_1 and W_2 are the masses of solvent and solute while M_1 and M_2 are their relative molecular masses receptively, then

$$n_1 = \frac{W_1}{M_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2}$$

$$\frac{\Delta p}{p^\circ} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}}$$

$$\frac{\Delta p}{p^\circ} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

$$M_2 = \frac{p^\circ}{\Delta p} \times \frac{W_2 M_1}{W_1}$$

The molecular mass (M_2) of a non-volatile solute can be calculated from the above equation.

Q14. Give graphical explanation for elevation of boiling point of a solution.

Describe one method to determine the boiling point elevation of a solution.

Elevation of Boiling Point

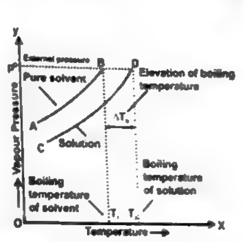
Boiling Point

The temperature at which the vapour pressure of a liquid becomes equal to the external pressure is called its boiling point.

The presence of a non-volatile solute in the solution decreases the vapour pressure of the solvent. Greater the concentration of solute, greater will be the lowering of vapour pressure. Therefore, the temperature at which a solvent in the solution state boils is increased.

Graphical explanation

In order to understand it, determine the vapour pressures of a solvent at various temperatures. Plot a graph between temperatures on x-axis and vapour pressures on y-axis. A rising curve is obtained with the increase of temperature.



Elevation of boiling temperature curve

The slope of the curve at high temperature is greater, which shows that at high temperature the vapour pressure increases more rapidly. Temperature T_1 on the curve AB which is for the pure solvent, correspond to the boiling point of the solvent. The solvent boils when its vapour pressure becomes equal to the external pressure represented by p°.

When the solute is added in the solvent and vapour pressures are plotted against temperatures, then a curve CD is obtained. This curve is lower than AB because vapour pressures of solution are less than those of pure solvent. Solution will boil at higher temperature T_2 to equalize its pressure to p°. The difference of two boiling points gives the elevation of boiling point ΔT_b.

Relationship between molality and ΔT_b

The higher the concentration of solute, the greater will be the lowering in vapour pressure of solution and hence higher will be its boiling point. So, elevation of boiling point ΔT_b is directly proportional to the molality of solution.

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m \qquad \text{......(i)}$$

where, K_b is ebullioscopic constant or molal boiling point constant.

According to eq. (i) molality of any solute determines the elevation of boiling point of a solvent.

Determination of molecular mass

We know that,

$$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

$$m = \frac{W_2}{M_2} \times \frac{1}{W_1/1000} = \frac{1000 W_2}{M_2 W_1}$$

Putting the value of 'm' from equation (i) into above equation.

$$\Delta T_b = K_b \frac{1000 W_2}{M_2 W_1}$$

or
$$M_2 = \frac{K_b}{\Delta T_b} 1000 \times \frac{W_2}{W_1}$$

This equation can be used to determine the molar mass of a non-volatile and non-electrolyte solute in a volatile solvent.

Measurement of Boiling Point Elevation (Landsberger's Method)

This is one of the best methods for the measurement of boiling point elevation of a solution.

Apparatus

The apparatus consists of four major parts:

(a) **An inner tube** with a hole in its side. This tube is graduated.

(b) **A boiling flask** which sends the solvent vapours into the graduated tube through a rosehead.

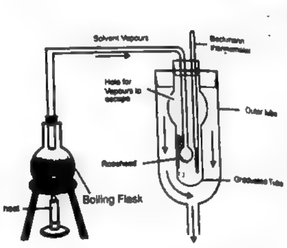
(c) **An outer tube**, which receives hot solvent vapours coming out from the side hole of the inner tube.

(d) **A thermometer** which can read upto 0.01 K.

Procedure

The solvent is placed in the inner tube. Some solvent is also taken in a separate flask and its vapours are sent into this tube. These vapours cause the solvent in the tube to boil by its latent heat of condensation. This temperature is noted which is the boiling point of the pure solvent.

The supply of the vapours is temporarily cut off and a weighed pellet of the solute is dropped in the inner tube. The vapours of the solvent are again passed through it until the solution is boiled. This temperature is again noted. Now the supply of the solvent vapours is cut off. The thermometer and the rosehead are removed and the volume of the solution is measured. The difference of the two boiling points gives the value of ΔT_b.



Landsberger method for measurement of elevation of boiling point

Calculation

The following formula is used to calculate the molecular mass of solute.

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{1000W_2}{W_1}$$

Q12. (a) Boiling point of solvent increases due to the presence of solutes:

Ans. "The boiling point is defined as the temperature at which the vapour pressure of liquid becomes equal to external pressure."

When a solute is added in solvent, then the vapour pressure of solvent lowers due to

(i) Interaction between solute-solvent particles.

(ii) Molecules of solute present at the surface hinder the evaporating tendency of solvent.

Hence, to equalize the vapour pressure of liquid with external pressure, more heat is to be supplied. So boiling point of solution is increased.

Example: Boiling point of pure water = 100°C

Boiling point of 1 molal urea solution in water = 100.52°C

Q12. (c) Boiling point of 1 molal urea solution is 100.52°C but boiling point of 2 molal urea solution is less than 101.04°C?

Ans. The conditions necessary to study the colligative properties are:

(i) Solution should be dilute.

(ii) Solute should be non-volatile.

(iii) Solute should be non-electrolyte.

One molal urea solution has a boiling point of 100.52°C but two molal urea solution has not twice the elevation of boiling point ($0.52 \times 2 = 1.04$°C) due to following reasons.

(i) The two molal solution is very concentrated so it does not fulfill the conditions of colligative properties.

(ii) Solute does not dissolve fully as rate of crystallization is greater than rate of dissolution.

(iii) Less molecules are free as most of them form clusters.

Hence 2 molal urea solution has a less elevation of boiling point than expected.

Q12. (d) Beckmann's thermometer is used to note the depression of freezing point.

Ans. As depression of freezing point or elevation of boiling points is very small in magnitude so a sensitive thermometer was developed by "Beckmann". It can read upto 1/100th of a degree Celsius or 0.01 K. It can detect a very little change in boiling point or freezing point much accurately. Therefore Beckmann thermometer is used to note the depression of freezing point.

Q15. Freezing points of solutions are depressed when non-volatile solutes are present in volatile solvents. Justify it. Plot a graph to elaborate your answer. Also, give one method to record the depression of freezing point of a solution.

Depression of Freezing Point of a Solvent by a Solute

"The temperature at which two physical states (solid and liquid) of any substance co-exist is called freezing point."

or

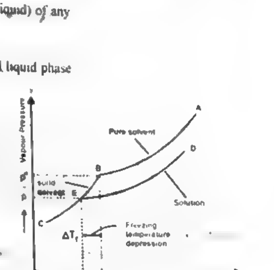
"The temperature at which the vapour pressure of solid and liquid phase become equal is called freezing point."

Explanation

When a non-volatile solute is added to a solvent, its vapour pressure decreases. At the freezing point, there are two things in the vessel i.e. liquid solution and the solid solvent. The solution will freeze at that temperature at which the vapour pressures of both liquid solution and solid solvent are same. It means that a solution should freeze at lower temperature than pure solvent.

Graphical Explanation

In order to understand it, plot a graph between vapour pressure and temperature for pure solvent and that of solution. The curve ABC is for the pure solvent. The solvent freezes at temperature T_1 corresponding to the point B when the vapour pressure of freezing solvent is p°.



Depression of freezing point curve

The portion of the curve BC is for the solid solvent. This portion has greater slope showing that the change of vapour pressure with the change of temperature is more rapid.

The curve DEC for the solution will meet the curve BC at the point E. This is the freezing point of solution T and corresponds to the vapour pressure p which is lower than p°. The reason is that vapour pressure of solution is less than that of pure solvent.

Depression of freezing point = freezing point of pure solvent − freezing point of solution

So, $\Delta T_f = T_1 - T_2$

Relationship between molality and ΔT_f

This depression of freezing point ΔT_f is related to the molality of the solution ... relationship is similar to that of elevation of boiling point.

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \quad \text{(i)}$$

Where, K_f is molal freezing point constant or cryoscopic constant.

Determination of molecular mass

We know that,

$$\text{Molality} = \frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$$

$$m = \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

Putting in eq. (i)

$$\Delta T_f = K_f\left(\frac{W_2}{M_2} \times \frac{1000}{W_1}\right)$$

$$\text{(Molar mass of solute)}\ M_2 = \frac{K_f}{\Delta T_f} \times \frac{W_2 1000}{W_1}$$

Measurement of Freezing Point Depression (Beckmann's Method)

Apparatus

The apparatus consists of three major parts:

(i) **A freezing tube with a side arm.** It contains solvent or solution and is fitted with a stirrer and a Beckmann's thermometer.

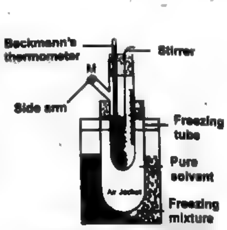
(ii) **An outer larger tube** into which the freezing tube is adjusted. The air jacket in between these tubes help to achieve a slower and more uniform rate of cooling.

(iii) A large jar containing a freezing mixture.

Procedure

Around 20 to 25 g of the solvent is taken in the freezing tube. The bulb of the thermometer is immersed in the solvent. First of all, approximate freezing point of the solvent is measured by directly cooling the freezing tube in the freezing mixture.

The freezing tube is then put in the air jacket and cooled slowly. In this way, accurate freezing point of the solvent is determined. Now the solvent is re-melted by removing the tube from the bath and weighed amount of 0.2 to 0.3 g of the solute is introduced in the side tube. The freezing point of the solution is determined while stirring the solution. The difference of the two freezing points gives the value of ΔT_f.



Backmann's freezing point apparatus

Calculation

The following formula is used to calculate the molar mass of solute.

$$M_2 = \frac{K_f}{\Delta T_f} \times \frac{1000W_2}{W_1}$$

Q12. (b) Freezing points are depressed due to the presence of solutes.

Ans. "The freezing point is defined as, the temperature at which the solid and the liquid phase of a substance has same vapour pressures."

When a non-volatile solute is dissolved in a solvent, its vapour pressure decreases due to solute-solvent interactions. Now the vapour pressure of the solution becomes equal to the solid solvent at a lower temperature than the pure solvent. Thus freezing points are depressed due to presence of solutes.

e.g.

Freezing point of pure water = 0°C

Freezing point of 1 molal glucose solution = −1.86°C

Applications of Boiling Point Elevation and Freezing Point Depression Phenomenon

(i) It is used to **determine the molar mass** of substances.

(ii) The study of colligative properties has contributed to the development of **solution theory**.

(iii) The presence of a solute increases the liquid range of the solution both by raising the boiling point and lowering the freezing point.

(iv) The most important application of this phenomenon is the use of an **antifreeze** in the radiator of an automobile. The solute is **ethylene-glycol** which is not completely miscible with water but has a very low vapour pressure and non-volatile in character. When mixed in water, it lowers the freezing point as well as raises the boiling point.

- During winter it protects a car by preventing the liquid in the radiator from freezing, as water alone, if it were used instead.
- In hot summer, the antifreeze solution also protects the radiator from boiling over.

(v) Another important application is the use of NaCl or KNO_3 to lower the melting point of ice. One can prepare a freezing mixture for use in an ice cream machine.

Q12. (e) In summer antifreeze solutions protect the liquid of radiator form boiling over?

Ans. Ethylene glycol is used as antifreeze in car radiator. When it is added into the water, it increases the liquid range of the solution by raising its boiling point and by lowering its freezing point.

In this way in hot summer the antifreeze solution protect the car radiator from boiling over.

Q12. (f) NaCl and KNO_3 are used to lower the melting point of ice?

Ans. NaCl and KNO_3 are electrolytes. They are added to water, to lower the vapour pressure of water. As these salts dissociate into ions in their aqueous solutions, therefore they have greater number of solute particles as compared to a solution of non-volatile non-electrolyte solute of same concentration.

$$NaCl \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$KNO_3 \rightleftharpoons K^+_{(aq)} + NO^-_{3(aq)}$$

Thus NaCl and KNO_3 solution have elevation of boiling point and depression of freezing point to a greater extent than that of non-volatile, non-electrolyte solutes. Therefore they are commonly used as a freezing mixture.

Q16. Discuss the energetics of solution. Justify the heats of solutions as exothermic and endothermic properties.

Energetics of Solution

"The energy changes involved during the formation of a solution are termed as energetic of solution."

Explanation

In a solution, the distances between solute and solvent molecules or ions increase somewhat as compared with their pure states. This increase in the distance of solvent molecules requires energy to overcome the cohesive intermolecular forces. Hence, it is an endothermic process. Similarly, the separation of solute molecules also needs energy so it is also an endothermic process. The intermixing of solute with solvent molecules is to establish new intermolecular forces between unlike molecules. It releases energy and thus is an exothermic phenomenon. The strengths of the two type of forces will decide whether the process of dissolution will be endothermic or exothermic.

Thus, the process of dissolution occurs with either an absorption or release of energy. This is due to breakage and re-establishment of intermolecular of intermolecular forces of attraction between solute and solvent molecules.

Heat of solution

"The quantity of heat energy, that is absorbed or released when a substance forms solution, is termed as heat of solution."

Examples

(i) When potassium nitrate is dissolved in water, the temperature of the solution decreases. It shows it to be an endothermic process.

$$KNO_{3(s)} + H_2O \rightarrow KNO_{3(aq)} \quad \Delta H = +35.7\,kJmol^{-1}$$

(ii) The solution of lithium chloride in water produces heat, showing that the process of dissolution is exothermic.

$$LiCl_{(s)} + H_2O \rightarrow LiCl_{(aq)} \quad \Delta H = -35.0\,kJmol^{-1}$$

Enthalpy of solution

"The heat change when one mole of the substance is dissolved in a specified number of moles of solvent at a given temperature is called enthalpy of solution (ΔH_{soln})."

Example

When one mole of sodium chloride (58.5g) is dissolved in 10 moles of water (180g), then 2.008 kJ of energy is absorbed.

$$NaCl + 10H_2O \rightarrow NaCl.10H_2O \quad \Delta H = +2.008\,kJ$$

The ΔH gives the difference between the energy possessed by the solution after its formation and the original energy of the components before their mixing i.e.

$$\Delta H_{solu} \quad H_{solution} \quad H_{components}$$

Heats of solution of some ionic solids

Substance	Heat of solution (kJ mol^{-1})
NaCl	4.98
NH_4NO_3	26.0
KCl	17.8
KI	21.4
NH_4Cl	16.2
LiCl	-35.0
Li_2CO_3	-12.8

Here, H_{solu} is the energy content of solution after its formation, while $H_{components}$ represents the energy contents of components before their mixing. However, both these factors can not actually be measured. Only their difference i.e the change ΔH_{solu} is practically measurable. If the value of ΔH_{solu} is negative, it would mean that the solution is having less energy than the components from which it was made, hence the dissolution process is an exothermic one. On the other hand, an endothermic process would have a positive ΔH_{solu} value

The magnitude of heat of solution gives information regarding the strength of intermolecular forces of attraction between components which mix to form a solution.

Hydration energies of common ions

Ion	ΔH° (kJ mole^{-1})
H^+	-1075
Li^+	-499
Na^+	-390
Ag^+	-464
K^+	-305
Mg^{2+}	-1891
Cu^{2+}	-1562
NH_4^+	-281
F^-	-457
Cl^-	-384
Br^-	-351
OH^-	-460

Hydraton Energy of Ions

When an ionic compound, say potassium iodide is dissolved in water, the first step is the separation of K^+ and I^- ions from solid. In the second step, these separated ions are surrounded by solvent molecules. The first step breaks the lattice to separate the ions. Since, energy is required to accomplish this step, so this step is endothermic.

Lattice energy

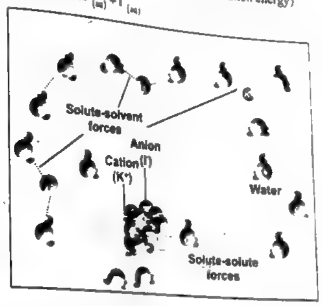
"The amount of energy needed to separate a crystalline compound into isolated ions (or atoms) is known as lattice energy."

- The lattice energy of ionic solids is always higher than molecular solids.

- In the second step, the ions are brought into water and get hydrated (solvated). A hydrated ion is attracted by the solvent dipoles and energy is released, so this step is exothermic.

The energy given out by this step is known as the hydration energy (or solvation energy)

$$K^+ + I^- + xH_2O \rightarrow K^+_{(aq)} + I^-_{(aq)}$$



Hydration energy

"The amount of energy released during hydration of one mole of an ionic compound in excess amount of water is called as hydration energy."

The final equation will be as follows

$$KI_{(s)} + xH_2O \rightarrow K^+_{(aq)} + I^-_{(aq)}$$

Relation between hydration energy and the size of ions

- It is interesting to compare hydration energies values of individual ions, i.e. cations and anions with their ionic radii. Greater the size of monovalent cation, lesser is the heat of hydration.
- Divalent and trivalent cations have higher values due to high charge densities
- Anions also show a definite trend of heat of hydration, depending upon their sizes

Preparation of and Infinitely dilute solution

On diluting a concentrated solution, there is a further heat change. This heat change depends on the amount of water used for dilution. The heat of dilution gradually decreases, so that eventually increasing the dilution produces no further heat change. This occurs when there are 800-1000 moles of water to one mole of solute. This stage is called infinite dilution and the heat of solution is expressed as:

$$NaCl_{(s)} + H_2O \longrightarrow NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}, \quad \Delta H_{soln} = +4.98\,kJ\,mol^{-1}$$

Hydration and Hydrolysis

Hydration

"The process in which water molecules surround and interact with solute ions or molecules is called hydration."

Explanation

When ionic compounds are dissolved in water, they are dissociated into ions. Negative ions, are surrounded by water molecules. The partial positively charged hydrogen atoms of water surround and attract the anions with electrostatic force of attraction. Similarly, positive ions of solute create attractions with partial negative oxygen atoms of water molecules. In this way, ions are hydrated.

Hydrated ions

The ions which are surrounded by water molecules are called hydrated ions." e.g. in case of dissolution of NaCl, Na^{+1} and Cl^{-1} are called hydrated ions.

Factors effecting hydration:

The number of water molecules, which surround a given ion depends upon:

(i) Size of ion (ii) Magnitude of charge

- If the size of ion is small, and is highly charged positive ion then it has high charge density. Hence, the greater number of water molecules surround it.
- Negatively charged ions have low charge density and have smaller number of water molecules surrounding them.

Conclusions

Hence, the ion with higher charge density has a greater ability to attract polar water molecules than ions with smaller charge density.

Hydrates

"Those crystalline substances which contain chemically combined water in a definite proportions are called hydrates."

Formation of hydrates

- Mostly hydrates are formed when aqueous solutions of soluble salt are evaporated.
- The formation of hydrates is not limited to salts but is common with acids, bases and elements.

Example: The water molecules are attached with cations in the hydrates. Anyhow, in $CuSO_4.5H_2O$, four water molecules are attached with Cu^{2+} and one with SO_4^{2-}. The reason is that Cu^{2+} is much smaller than SO_4^{2-}, which has same amount of charge.

Water of Crystallization

"Those water molecules which combine with substances as they are crystallized from aqueous solutions are called water molecules of crystallization or water of hydration."

Examples

(i) $(COOH)_2.2H_2O$ (Oxalic acid) (ii) $MgCl_2.6H_2O$ (iii) $Na_2B_4O_7.10H_2O$ (Borax)
(iv) $CaSO_4.2H_2O$ (Gypsum) (v) $MgSO_4.7H_2O$ (Epsom salt) (vi) $BeCl_2.2H_2O$
(vii) $Na_2CO_3.10H_2O$

Hydrolysis

"The interactions between salts and water are called hydrolytic reactions and this phenomenon is called hydrolysis."

Salts are of following types:

(a) Acidic salts
(b) Basic salts
(c) Neutral salts

When NaCl is dissolved in water, the resulting solution is neutral i.e. the concentration of H^+ and OH^- ions are equal to 10^{-7} mol dm^{-3}, as in pure water. But this balance between H^+ and OH^- ions can be disturbed with resulting change in the pH of solution when other salts are dissolved in water.

(a) Acidic salts

"The salts which are formed by the reactions of weak bases and strong acids are called acidic salts."

or

"The salts which lower the pH of water less than 7 are called acidic salts."

Examples

NH_4Cl, $AlCl_3$ and $CuSO_4$ give acidic solutions in water.

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ + 3Cl^-$$

$$CuSO_4 + 2H_2O \rightleftharpoons Cu(OH)_2 + 2H^+ + SO_4^{2-}$$

These hydrolytic reactions produce weak bases $Al(OH)_3$, NH_4OH, $Cu(OH)_2$. But, Cl^- and SO_4^{2-} are weal conjugate bases of HCl and H_2SO_4. These are not hydrolyzed in water. H^+ ions remain free in solution and so thei solutions are acidic in character.

The K_a values of HCl and H_2SO_4 are very high as compared to K_b values of $Al(OH)_3$, NH_4OH and $Cu(OH)$ It should be kept in mind cationic part of acidic salt will hydrolyse.

(b) Basic salts

"Those salts which are formed by the reaction of strong bases and weak acids are called basic salts."

or

"Those salts which increase the pH of water more than 7 are called basic salts."

Examples

Na_2CO_3 and CH_3COONa form basic solutions in water.

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

The acetate ion is hydrolyzed in water to give CH_3COOH and OH^- ions become free. Na^+ ion is not hydrolysed. The result is that the solution becomes basic in nature. Similarly, Na_3PO_4 and Na_3AsO_4 etc. give basic solutions in water due to formation of Na^+, OH^- and weak acids H_3PO_4 and H_3AsO_4, which are least dissociated.

(c) Neutral Salts

(i) Salts from strong acids and strong bases

The dissolution of KCl, NaCl, Na_2SO_4, KBr etc. in water give neutral solutions. Because these salts are not hydrolysed in water. Their positive ions K^+, Na^+ are not hydrolysed by water. Similarly their negative ions Cl^-, Br^-, SO_4^{-2} are not hydrolysed.

(ii) Salts from weak acids and weak bases

The salts derived from weak acids and weak bases may not give neutral solutions. It depends upon the pK_a and pK_b values of acids and base produced.

Key Points

1. A solution, on average, is a homogeneous mixture of two or more kinds of different molecular or ionic substances. The substance, which is present in a large quantity is called a solvent and the other in small quantity is, called a solute.
2. Solutions containing relatively lower concentrations of solute are called dilute solutions, whereas those containing relatively higher concentrations of solutes are called concentrated solutions. Solubility is the concentration of a solute in a solution, when the solution is at equilibrium with the solute at a particular temperature.
3. The concentration of a solution may be expressed in a number of ways.
4. Solutions may be ideal or non-ideal. Those solutions, which obey Raoult's law are ideal solutions. Raoult's law tells us that the lowering of vapour pressure of a solvent by a solute, at a constant temperature, is directly proportional to the concentration of solute.
5. Many solutions do not behave ideally, as they show deviations from Raoult's law. A solution may show positive or negative deviation from Raoult's law. Such liquid mixtures, which distill without change in composition, are called azeotropic mixtures.
6. Colligative properties of a solution are those properties, which depend on the number of solute and solvent molecules or ions and are independent of the nature of solute. Lowering of vapour pressure, elevation of boiling point and depression of freezing point and osmotic pressure are the important colligative properties of solutions.

7. Elevation of boiling point of a solvent in one molal solution is called molal boiling constant or ebullioscopic constant. Depression of freezing point of a solvent in one molal solution is called molal freezing point constant or cryoscopic constant.

8. The enthalpy or heat of solution of a substance is the heat change when one mole of the substance is dissolved in a specified number of moles of solvent at a given temperature.

9. The process in which water molecules surround and interact with solute ions or molecules of water in their crystal lattices, are called hydrates. They are mostly produced, when aqueous solutions of soluble salts are evaporated.

10. Salts of weak acids with strong bases react with water to produce basic solutions, whereas slats of weak bases with strong acids react to give acidic solutions. Such reactions are called hydrolytic reactions, and the salts are said to be hydrolysed. Salts of strong acids and strong bases do not hydrolyse and give solution.

SOLVED OBJECTIVE EXERCISE

Q1: Choose the correct answer of the following:

(i) Molarity of pure water is:
(a) 1 (b) 18
(c) 55.5 (d) 6

(ii) 18 g glucose is dissolved in 90 g water. The relative lowering of vapour pressure is equal to:
(a) 1/5 (b) 5.1
(c) 1/51 (d) 6

(iii) A solution of glucose is 10% w/v. The volume in which 1 g mole of it is dissolved will be:
(a) 1 dm^3 (b) 1.8 dm^3
(c) 200 cm^3 (d) 900 cm^3

(iv) An aqueous solution of ethanol in water may have vapour pressure:
(a) Equal to that of water (b) Equal to that of ethanol
(c) More than that of water (d) Less than that of water

(v) An azeotropic mixture of two liquids boils at a lower temperature than either of them when:
(a) It is saturated
(b) It shows positive deviation from Raoult's Law
(c) It shows negative deviation from Raoult's Law
(d) It is metastable

(vi) In azeotropic mixture, showing positive deviation from Raoult's law, the volume of the mixture is:
(a) Slightly more than total volume of components
(b) Slightly less than total volume of components
(c) Equal to total volume of components
(d) None of these

(vii) Which of the following solutions has the highest boiling point:
(a) 5.85% NaCl (b) 18% glucose solutions
(c) 6% urea solution (d) All have some the boiling point

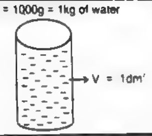
(viii) Two solutions of NaCl and KCl are prepared separately by dissolving same amount of solute in water. Which of the following statements is false for these solutions:

(a) KCl solution will have higher boiling point than NaCl.
(b) Both the solution have different boiling point.
(c) KCl and NaCl solution possess same vapour pressure
(d) KCl solution possess lower freezing point than NaCl solution.

(ix) Molal boiling point constant is the ratio of elevation in boiling point to:
(a) Molarity (b) Molality
(c) Mole fraction (d) None of these

(x) Colligative properties are properties of:
(a) Dilute solutions which behave ideally (b) Concentrated solutions which behave non-ideally
(c) Both (a) and (b) (d) Neither (a) nor (b)

Solved Exercise MCQ's

Q. No	Answer	[illegible]	
(i)	(c) 55.5	$\frac{1000g}{18g\ mol^{-1}} = 55.5$ mol So molarity of water is 55.5 mol dm^{-3}	m = 1000g = 1kg of water 
(ii)	(c) 1/51	$\frac{\Delta p}{p^\circ} = x_2$ (Mole fraction of Solute) Glucose is solute and water is solvent here. Mass of glucose = 18g Mass of water = 90g $n_{glucose} = \frac{18}{180} = 0.1$ mol $n_{water} = \frac{90}{18} = 5$ mol $n_t = n_{glucose} + n_{water} = 0.1 + 5 = 5.1$ $x_{glucose} = \frac{0.1}{5.1} = \frac{1}{51}$	
(iii)	(b) 1.8 dm^3	10% $^w/_v$ glucose solution means 10g of glucose present in solution = 100 cm^3 1g mol (180g) of glucose present in solution = $\frac{100}{10} \times 180$ = 1800 cm^3 = 1.8 dm^3	
(iv)	(c) More than that of water	We know that boiling point $\propto \frac{1}{\text{Vapour Pressure}}$ Boiling point of ethanol = 78.5°C Boiling point of water = 100°C So an aqueous solution of ethanol in water may have vapour pressure more than that of water.	

(v)	(b) It shows positive deviation from Raoult's Law	Ethanol-water mixture is an example of non ideal solution showing positive deviation from Raoult's Law. It boils at 78.1°C with 4.5% water and 95.5% alcohol. 78.1°C is lower than the boiling point of ethanol (78.5°C) and water (100°C).
(vi)	(a) Slightly more than total volume of components	Two liquids A and B forming Azeotropic mixture showing positive deviation from Raoult's Law. A-B attractive force should be weaker than A-A and B-B attractive forces. 'A' and 'B' have different shape, size and character. So the volume of solution is slightly greater than total volume of components.
(vii)	(a) 5.85% NaCl	Greater the number of solute particles, higher will be the boiling point. $5.85\%\ NaC = 1\dfrac{5.85}{58.5} \times N_A = 6.022 \times 10^{22}\ NaCl$ $NaCl \rightleftharpoons Na^+ + Cl^-$ So Solute particles are 1.2×10^{23}.
(viii)	(c) KCl and NaCl solutions possess same vapour pressure.	If we take same amount of NaCl (molar mass = 58.5) and KCl (molar mass = 74.5) then number of particles of NaCl will be more than KCl. Hence, the solution of both solutes will show different values of colligative properties.
(ix)	(b) Molality	$\Delta T_b \propto m$ $\Delta T_b = K_b m$ $K_b = \Delta T_b / m$
(x)	(a) Dilute solutions which behave ideally	Those properties of a solution which depend upon the number of solute and solvent molecules or ions and are independent of the nature of the solute are called colligative properties.

Q2: Fill in the blanks with suitable words:

(i) Number of molecules of sugar in 1 dm^3 of 1 M sugar solution is ________.

(ii) 100 g of 10% aq. solution of NaOH Contains 10 g NaOH in ________ g of water.

(iii) When an azeotropic mixture is distilled its ________ remains constant.

(iv) The molal freezing point constant is also called ________.

(v) Boiling point of an azeotropic solution of two liquid is lower than either of them because the solution show ________ from Raoult's law.

(vi) Among equimolal aqueous solutions of NaCl, $BaCl_2$ and $FeCl_3$, the maximum depression of freezing point is shown by ________ solution.

(vii) A solution of ethanol in water shows ________ deviation and gives azeotropic solution with ________ boiling point than other components.

(viii) Colligative properties are used to calculate ________ of a compound.

(ix) The hydration energy of Br^- ion is ________ than that of F^- ion.

(x) The aqueous solution of NH_4Cl is ________ while that of Na_2SO_4 is ________.

ANSWERS

(i) 6.02×10^{23}	(ii) 90 g	(iii) composition
(iv) cryoscopic constant	(v) positive deviation	(vi) $FeCl_3$
(vii) Positive, low	(viii) molar mass	(ix) less
(x) acidic, neutral		

Q3: Indicate True and False from the given statement:

(i) At a definite temperature the amount of solute in a given saturated solution is fixed.

(ii) Polar solvents readily dissolve non-polar covalent compounds.

(iii) The solubility of a substance decreases with increase in temperature, if the heat of a solution is negative.

(iv) The rate of evaporation of liquid is inversely proportional to the intermolecular forces of attraction.

(v) The molecular mass of an electrolyte determined by lowering of vapour pressure is less than the theoretical molecular mass.

(vi) Boiling point elevation is directly proportional to the molality of solution and inversely proportional to boiling point of solvent.

(vii) All solutions containing 1 g non-volatile, non electrolyte solute in same solvent will have the same freezing point.

(viii) The freezing point of a 0.05 molal solution of a non-volatile, non-electrolyte solute in water is –0.093 C°

(ix) Hydration and hydrolysis are different process for Na_2SO_4.

(x) The hydration energy of an ion only depends upon its charge.

ANSWERS

(i) True	(ii) False	(iii) True	(iv) True	(v) True
(vi) True	(vii) False	(viii) False	(ix) True	(x) False

NUMERICALS OF EXERCISE

Q17. (a) Calculate the molarity of glucose solution when 9 g of it are dissolved in 250 cm^3 of solution?

Ans. **Given data:**

Mass of glucose = m = 9.0 g

Volume of solution = V = 250 cm^3 = 0.25 dm^3

Molar mass of glucose = M = 180 g mol^{-1}

Required:

Molarity = ?

Solution:

$$\text{Molarity} = \frac{\text{mass of solute in g}}{\text{Mol. mass of solute}} \times \frac{1}{\text{Vol. in dm}^3}$$

$$\text{Molarity} = \frac{9}{180 \times 0.25} = 0.2\ mol\ dm^{-3}$$

Molarity of solution = 0.2 M

Q17. (b) Calculate the mass of urea in 100 g of water in 0.3 molal solution.

Ans. **Given data:**

Mass of water = 100 g = 0.1 kg

Molality of solution = 0.3 mol kg^{-1}

Molar mass of urea (NH_2CONH_2) = $14 + 1 \times 2 + 12 + 16 + 14 + 2 \times 1$

= $14 + 2 + 12 + 16 + 14 + 2 = 60 g\ mol^{-1}$

Required:

Mass of urea in g = ?

Solution:

Molality $= \frac{\text{mass in g of solute}}{\text{Mol. mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$

Mass (g) of solute = Molality × mol. mass × mass of solvent in kg (of solute)

$= 0.3 \times 60 \times 0.1 = 1.8$ g

Mass of urea in g = 1.8 g

Q17. (c) Calculate the conc. of a solution in mol kg^{-1} which is obtained by mixing 250 g of 20 % NaCl with 200 g of 40 % solution.

Ans.

(i) **Given data:**

Percentage of composition of NaCl solution = 20 %

Mass of 20 % solution = 250 g

(ii) Percentage composition of 2^{nd} solution = 40 %

Mass of 2^{nd} solution = 200 g

Molar mass of NaCl = 58.5 g mol^{-1}

Required:

Molality of solution which is obtained by mixing solution (i) and solution (ii) = ?

Solution:

To calculate Molality, first we will find amount of NaCl in both solution as follow:

(i) **Solution (i): 20 % NaCl solution:**

100 g of solution has quantity of NaCl = 20 g

1 g of solution has quantity of NaCl $= \frac{20}{100}$ g

250 g of solution has quantity of NaCl $= \frac{20}{100} \times 250$

= 50 g

Amount of solute = 50 g

Amount of solvent = 250 − 50 = 200 g

(ii) **Similarly for 40 % NaCl solution.**

100 g of solution has quantity of NaCl = 40 g

1 g of solution has quantity of NaCl $= \frac{40}{100}$ g

200 g of solution has quantity of NaCl $= \frac{40}{100} \times 200$

= 80 g

Amount of solute = 80 g

Amount of solvent = 200 − 80 = 120 g

(iii) Now we can calculate molality by data calculated above:

Calculated data:

Mass of solute in sol (i) = 50 g

Mass of solute in sol (ii) = 80 g

Total mass of solute = 50 + 80 = 130 g

Mass of solvent in sol (i) = 200 g

Mass of solvent in sol (ii) = 120 g

Total mass of solvent = 200 + 120 = 320 g

= 0.320 kg

Molality $= \frac{\text{mass of solute in g}}{\text{Mol. mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$

$= \frac{130}{58.5} \times \frac{1}{0.32} = 6.94$ molal

Molality = 6.94 molal

Q18. (a) An aqueous solution of sucrose has been labeled as one molal. Find the mole fraction of solute and solvent:

Ans. **Given data:**

Molality of solution = 1 mol kg^{-1}

Required:

Mole fraction of solute = ?

Mole fraction of solvent = ?

Solution:

As one molal solution means 1 mol solute dissolved per 1000 g of H_2O

So 342 g (mol. mass of sucrose) dissolved per 1000 g of H_2O.

We can calculate no. of moles of each component.

no. of moles $= \frac{\text{mass in g}}{\text{Molar mass}}$

(i) n_2 = moles of sucrose $= \frac{342 \text{ g}}{342 \text{ g mol}^{-1}} = 1$ mol

(ii) n_1 = moles of water $= \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.55$ mol

(iii) n_t = Total moles $= n_1 + n_2 = 55.55 + 1 = 56.55$ mol

(iv) Mole fraction $= \frac{\text{moles of a component}}{\text{Total moles}}$

So $X_1 = \frac{n_1}{n_t}$, $X_2 = \frac{n_2}{n_t}$

(a) mole fraction of sucrose $= \frac{1}{56.55} = 0.0176$

(b) mole fraction of water $= \frac{55.55}{56.55} = 0.9823$

So

mole fraction of solute = 0.0176

mole fraction of water = 0.9823

Q18. (b) You are provided by 80 % H_2SO_4 with density of 1.8 g cm^{-3}. How much vol. of this solution is required to prepare 1 dm^3 of 20 % H_2SO_4 with density 1.25 g cm^{-3}.

Ans. **Given data:**

Solution (i) has purity = 80% H_2SO_4

Density of sol (i) = 1.8 g cm^{-3}

Solution (ii) has = 20% H_2SO_4

Density of solution (ii) = 1.25 g cm^{-3}

Required:

Vol. of sol (i) to prepare sol (ii) = ?

Solution:

Two steps are involved

(a) Finding Molarity of both solutions.

(b) Finding Vol. of sol (i) by formula of dilution

(a) Finding Molarity:

Solution (i)

From density we can calculate the mass of 1 dm^3 (1000 cm^3) of solutions.

1 cm^3 H_2SO_4 contains mass = 1.8 g $\left[\begin{array}{c} d = \dfrac{m}{v} \\ \text{or } m = d \times v \end{array}\right]$

So 1000 cm^3 = 1.8 × 1000

= 1800 g

% purity of H_2SO_4 = 80 %

100 g H_2SO_4 contains pure acid = 80 g

1 g H_2SO_4 contains pure acid $= \frac{80}{100}$

1800 g H_2SO_4 containing pure acid $= \frac{80}{100} \times 1800$

= 1440 g

No. of moles of H_2SO_4 $= \frac{\text{mass of pure } H_2SO_4}{\text{mol. mas of } H_2SO_4}$

$= \frac{1440}{98} = 14.7$ mol

So Molarity of solution (i) = 14.7 M

Similarly for solution (ii)

1 cm^3 H_2SO_4 solution contains mass of acid = 1.25 g

1000 cm^3 H_2SO_4 solution contains = 1.25 × 1000

= 1250 g

Purity of acid = 20 %

so

100 g of acid contains pure acid = 20 g

1 g of acid contain mass of acid $= \frac{20}{100}$

1250 g of acid contain mass of acid $= \frac{20}{100} \times 1250$

= 250 g

No. of moles of H_2SO_4 $= \frac{\text{mass of pure acid}}{\text{mol. mass}}$

$= \frac{250}{98.0} = 2.55$ mol

So molarity of solution (ii) = 2.55 mol dm^{-3}

(b) **Calculation of volume:**

Data: Molarity of sol (i) $= M_1 = 14.7$ M

Molarity of sol (ii) $= M_2 = 2.55$ M

Volume of sol (ii) to be prepared $= V_2 = 1$ dm^3

Required:

Volume of sol (i) to be diluted $= V_1 = ?$

Solution:

Formula for dilution is

$M_1V_1 = M_2V_2$

$V_1 = \frac{M_2V_2}{M_1} = \frac{2.55 \times 1000}{14.7}$

$= 173.46 = 173.5 \text{ cm}^3$

173.5 cm^3 of 80 % H_2SO_4 is diluted upto 1000 cm^3 in a measuring flask to prepare 20 % H_2SO_4.

Q19. **250 cm^3 of 0.2 MK_2SO_4 is mixed with 250 cm^3 of KCl solution. Calculate the mol. concentration of K^+ in solution.**

Ans. **Given data:**

Molarity of K_2SO_4 = 0.2 molar

Molarity of KCl = 0.2 molar

Volume of solution (i) = 250 cm^3

Volume of solution (ii) = 250 cm^3

Volume after mixing = 500 cm^3

Required:

Concentration of K^+ ions = ?

Solution:

As both solutions are electrolytes they split up into ions on dissolution

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{-2}$$

$$KCl \rightleftharpoons K^+ + Cl^-$$

So 0.2 molar K_2SO_4 produces 0.4 molar K^+ ions and 0.2 molar KCl produce 0.2 molar K^+ ions.

Total K^+ = 0.4 + 0.2

= 0.6 molar

Total K^+ = 0.6 mole K^+/1000 cm^3

as our solution is 500 cm^3 therefore

1000 cm^3 of solution contains K^+ ion = 0.6 mol

1 cm^3 of solution contain K^+ ions $= \frac{0.6}{1000}$

500 cm^3 of solution contains $= \frac{0.6}{1000} \times 500$

= 0.3 mol K^+ ions

Amount of K^+ ions = 0.3 mol K^+ ions

Q20. **5 g of NaCl is dissolved in 1000 g of H_2O. Density of Solution is 0.997 g cm^{-1}. Calculate molarity, molality and mole fraction of this solution. Assume that volume of solution is equal to that of solvent.**

Ans. **Given data:**

Mass of NaCl = 5 g

Mass of H_2O = 1000 g = 1 kg

Density of sol. $= 0.997\ g\ cm^{-3}$

Required:

(a) Molality = ?

(b) Molarity = ?

(c) Mole fraction = ?

Solution:

(a) Molality

$$= \frac{\text{mass of solute in g}}{\text{mol. mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$$

$$= \frac{5}{58.5} \times \frac{1}{1} = \mathbf{0.08547\ molal}$$

(b) For molarity firstly volume of solution is to be calculate:

Mass of solute $= 5\ g$

Mass of solvent $= 1000\ g$

Total mass $= 1005\ g$

Density of solution $= 0.997\ g\ cm^{-3}$

Volume of solution = ?

$$d = \frac{m}{v} \quad \text{or} \quad V = \frac{m}{d}$$

$$V = \frac{1005}{0.997} = 1008.02\ cm^3 = 1.008\ dm^3$$

$$\text{Molarity} = \frac{\text{mass of solute}}{\text{mol. mass of solute}} \times \frac{1}{\text{vol. in dm}^3}$$

$$= \frac{5}{58.5} \times \frac{1}{1.008} = 0.0847$$

$$= \mathbf{0.085\ M}$$

(c) Mole fraction

$$\text{No. of mole of NaCl, } n_1 = \frac{\text{mass of NaCl}}{\text{molar mass}}$$

$$= \frac{5g}{58.5} = 0.0854\ \text{mol.}$$

$$\text{No. of moles of } H_2O,\ n_2 = \frac{\text{mass of } H_2O}{\text{Molar mass}}$$

$$= \frac{1000}{18} = 55.55\ \text{mol.}$$

n_t = Total moles = 55.55 + 0.0854 = 55.6354

$$\text{Mole fraction of NaCl} = \frac{\text{moles of NaCl}}{\text{Total moles}}$$

$$= \frac{0.0854}{55.6354} = \mathbf{0.001534}$$

$$\text{Mole fraction of } H_2O = \frac{55.55}{55.6354} = \mathbf{0.9984}$$

Molality = 0.08547 molal

Molarity = 0.085 molar

Mole fraction of NaCl: 0.00153

Mole fraction of H_2O: 0.9984

Q21. 4.675 g of a compound with empirical formula C_3H_3O was dissolved in 212.5 g of pure benzene. Freezing point ... was found to be 1.02°C less that pure benzene. Molal freezing point constant of benzene is 5.1°C. Calculate the (a) Relative molar mass (b) Molecular formula of compound.

Ans. Given data:

Mass of solute W_2 $= 4.675\ g$

Mass of solvent W_1 $= 212.5\ g$

ΔT_f (Depression in freezing point) $= 1.02°C$

K_f $= 5.1°C$

Empirical formula $= C_3H_3O$

Empirical formula mass $= 55\ g\ mol^{-1}$

Required:

(a) M_2 = ?

(b) Molecular formula of solute = ?

Solution:

(a) For molar mass

$$M_2 = \frac{K_f}{\Delta T_f} \times 1000 \times \frac{W_2}{W_1}$$

$$= \frac{5.1}{1.02} \times 1000 \times \frac{4.675}{212.5}$$

$$= 110\ g\ mol^{-1}$$

(b) For molecular formula = n × Empirical formula

$$\text{or} \quad n = \frac{\text{Molecular formula mas}}{\text{Empirical formula mass}}$$

$$= \frac{110}{55} = 2$$

So molecular formula is $= 2(C_3H_3O)$

i.e., $C_6H_6O_2$

Molar mass 110 g mol^{-1}

Molecular formula: $C_6H_6O_2$

Q22. Boiling point of a solution containing 0.2 g of a substance 'A' in 20 g of ether is 0.17 k higher then pure ether. Calculate the molar mass of 'A'.

Ans. Given data:

Mass of solute W_2 $= 0.2\ g$

Mass of solvent W_1 $= 20\ g$

ΔT_b $= 0.17\ K$

K_b $= 2.16\ K$

Required:

M_2: Molar mass of solute = ?

Solution:

$$M_2 = \frac{K_b}{\Delta T_b} \times 1000 \frac{W_2}{W_1}$$

$$= \frac{2.16}{0.17} \times 1000 \times \frac{0.2}{20}$$

$$= 127.05\ g\ mol^{-1}$$

Molar mass of solute : 127.05 g mol^{-1}

Q23. 3g of a non-volatile, non-electrolyte solute 'X' is dissolved in 50 g of ether (mol mass 74) at 293 K. Vapour pressure of ether falls from 442 torr to 426 torr at these condition. Calculate the molar mass of solute 'X'.

Ans. **Given data:**

Mass of solute = W_2 = 3g

Mass of solvent = W_1 = 50 g

Molar mass of solvent: M_1 = 74 g mol^{-1}

Vapour pressure of pure solvent P° = 442 torr

Vapour pressure of solvent in solution P = 426 torr

$\Delta P = P^\circ - P = 442 - 426$

$= 16$ torr

Required:

$M_2 = ?$

Solution:

$$M_2 = \frac{P^\circ}{\Delta p} \times \frac{W_2 M_1}{W_1}$$

$$M_2 = \frac{442}{16} \times \frac{3 \times 74}{50}$$

$= 122.65$ g mol^{-1}

Molar mass of solute = 122.65 g mol^{-1}

SOLVED EXAMPLES

Example (1):

Calculate the percentage by weight of NaCl, if 2.0g of NaCl is dissolved in 20g of water.

Ans. **Given Data:**

Weight of NaCl = 2.0g

Weight of solvent = 20g

Weight of solution = 20 + 2.0 = 22g

Required:

Percentage of NaCl by weight = ?

Solution:

Formula

$$\text{\% of NaCl by weight} = \frac{\text{Weight of NaCl}}{\text{Weight of solution}} \times 100$$

$$= \frac{2.0g}{22g} \times 100$$

% of NaCl by weight = 9.09% **Answer**

Example (2):

Calculate the molarity of a solution containing 20.7g of K_2CO_3 dissolved in 500cm^3 of the given solution.

Ans. **Given Data:**

Mass of K_2CO_3 = 20.7g

Molar mass of K_2CO_3 = 39 × 2 + 12 + 16 × 3

= 138g/$mole^{-1}$

Volume of solution = $500cm^3 = \frac{500}{1000} dm^3 = 0.5dm^3$

Required:

Molarity of solution = ?

Solution:

Formula

$$\text{Molarity} = \frac{\text{Mass of Solute}}{\text{Molar Mass of Solute}} \times \frac{1}{\text{Volume of solution in } dm^3}$$

$$\text{Molarity} = \frac{20.7g}{138g\ mol^{-1}} \times \frac{1}{0.5dm^3}$$

Molarity = 0.3 mol dm^{-3}

Example (3):

What is the molality of a solution prepared by dissolving 5g of toluene ($C_6H_5CH_3$) in 250g of Benzene.

Ans. **Given Data:**

Mass of Toluene = 5g

Mass of Benzene = $250g = \frac{250}{1000} = 0.25kg$

Molar Mass of Toluene $C_6H_5CH_3$ = 12 × 7 + 8 × 1 = 92g/mole

Required:

molality of Solution = ?

Solution:

Formula

$$\text{molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in Kg}}$$

$$\text{molality (m)} = \frac{5g}{92g mol^{-1}} \times \frac{1}{0.250kg}$$

$= 0.217$ mol kg^{-1}

molality of solution = 0.217 mol kg^{-1} **Answer**

Example (4):

Calculate mole fraction and mole percentage of each component in a solution having 92g ethyl alcohol, 96g of methyl alcohol and 90g of water.

Ans. **Given Data:**

Mass of enthyl alcohol (C_2H_5OH) = 92g

Mass of methyl alcohol (CH_3OH) = 96g

Mass of water (H_2O) = 90g

Required:

Mole fraction of $C_2H_5OH = X_{ethyl\ alcohol} = ?$

Mole fraction of $CH_3OH = X_{Methl\ alcohol} = ?$

Mole fraction of $H_2O = X_{water} = ?$

Mole % of ethyl alcohol = ?

Mole % of methyl alcohol = ?

Mole % of water = ?

Solution:

First of all get the number of moles of each component

$$\text{Number of Mole of the substance} = \frac{\text{Mass in grams of the substance}}{\text{Molecular Mass in gram}}$$

Molar Mass of ethyl alcohol (C_2H_5OH) = 12 × 2 + 1 × 5 + 16 × 1 + 1

= 24 + 5 + 16 + 1 = 46g mol^{-1}

$$\text{Number of mole ethyl alcohol} = \frac{92g}{46g\ mol^{-1}} = 2\text{moles}$$

Molar mass of methyl alcohol (CH_3OH) = 12 + 4 + 16 = 32g mol^{-1}

Number of moles of methyl alcohol = $\frac{96g}{32g\,mol^{-1}}$ = 3 moles

Molar mass of water (H_2O) = 2 + 16 = 18g mol^{-1}

Number of moles of water = $\frac{90g}{18g\,mol^{-1}}$ = 5moles

The mole fraction of any components is ratio of its moles to total number of moles.

$X_{\text{ethyl alcohol}} = \frac{2}{2+3+5} = \frac{2}{10} = 0.2$

$X_{\text{methyl alcohol}} = \frac{3}{2+3+5} = \frac{3}{10} = 0.3$

$X_{\text{water}} = \frac{5}{2+3+5} = \frac{5}{10} = 0.5$

Mole percentage of component is obtain by multiplying the mole fraction with 100.

Mole % of ethyl alcohol = 0.2 × 100 = **20**

Mole % of methyl alcohol = 0.3 × 100 = **30**

Mole % of water = 0.5 × 100 = **50**

Example (5):

Sea water has 5.65 × 10^{-3}g of dissolved oxygen in one kg of water. Calculate the concentration of oxygen in sea water in parts per million.

Ans. **Given Data:**

Mass of oxygen = 5.65 × 10^{-3}g

Mass of water = 1kg = 10^3g

Required:

Parts per million of oxygen = ?

Solution:

Formula:

$$\text{Parts per million (PPm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

$$\text{PPm of oxygen in sea water} = \frac{5.65 \times 10^{-3}g}{1000g} \times 10^6$$

Part per million of oxygen = **5.65**

Example (9):

The vapour pressure of water at 30 °C is 28.4 torr. Calculate the vapour pressure of a solution containing 70g of cane sugar ($C_{12}H_{22}O_{11}$) in 1000g water at same temperature. Also calculate the lowering of vapour pressure.

Ans. **Given Data:**

Vapour pressure of water = 28.4torr

Mass of sugar cane = 70g

Mass of H_2O in solution = 1000g

Molar mass of $C_{12}H_{22}O_{11}$ = 12 × 12 + 1 × 11 + 16 × 11

= 144 + 22 + 176 = 342g mol^{-1}

Molar mass of H_2O = 18.02g/mole

Required:

Vapour pressure of solution = ?

Lowering of vapour pressure = ?

Solution:

$$\text{Number of moles of compound} = \frac{\text{Mass}}{\text{Molar Mass}}$$

Number of moles of sugar $C_{12}H_{22}O_{11} = n_2 = \frac{70g}{342g\,mol^{-1}}$

= 0.20 moles

Number of moles of water $H_2O = n_1 = \frac{1000g}{18.02g\,mol^{-1}}$

= 55.49moles

Total number of moles = $n_1 + n_2$

= 0.20 + 55.49

= 55.69moles

Mole fraction of sugar = $X_2 = \frac{n_2}{n_1 + n_2}$

$= \frac{0.20}{55.69} = 0.0036$

Mole fraction of water = $X_1 = \frac{n_1}{n_1 + n_2}$

$= \frac{55.49}{55.69} = 0.9964$

Applying formula for vapour pressure of solution

$P = P^oX_1 = (28.4)(0.9964) = 28.29$torr

So, vapour pressure of solutions = **28.29**

Lowering of vapour pressure = 28.4 – 28.29

= 0.11 torr

Example (10):

Pure benzene has a vapour pressure of 122.0torr at 32°C. When 20g a non-volatile solute were dissolved in 300g of benzene, a vapour pressure of 120 torr was observed calculate the molecular mass of the solute. The molecular mass of benzene being 78.1

Given Data:

Mass of solute dissolved = W_2 = 20g

Vapour pressure of pure solvent = P^o = 122.0 torr

Vapour pressure of solution = P = 120 torr

Lowering of vapour pressure = ΔP = 122.0 – 120 = 2.0torr

Molar Mass of solvent = M_1 = 78.1

Mass of Solvent = W_1 = 300g

Required:

Molar Mass of solute = M_2 = ?

Solution:

We know that

$$\frac{\Delta p}{p^o} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

$$M_2 = \frac{p^o}{\Delta p} \times \frac{W_2 M_1}{W_1}$$

Putting the values

$$M_2 = \frac{122.0\text{ torr}}{2.0\text{ torr}} \times \frac{20g \times 78.1g\,mol^{-1}}{300g}$$

$= 317.6g\,mol^{-1}$

Molar Mass of solute = 317.6g mol^{-1}

Example (11):

The boiling point of water is 99.725 °C. To a sample of 600g of water are added 24.0 of a solute having molecular mass of 58g/mole, to form a solution. Calculate the boiling point of the solution.

Ans. **Given Data:**

Boiling point of pure water = 99.725 °C
Mass of solvent water = W_1 = 600g
Mass of solute = W_2 = 24.00g
Molar Mass of solute = M_2 = 58g mol^{-1}
The molar boiling point constant = K_b = 0.52 °C

Required:

Boiling point of the solution = ?

Solution:

Formula

$$\Delta T_b = K_b \times \frac{W_2}{M_1 \times M_2} \times 1000$$

$$= \frac{0.52 \times 24.00}{600 \times 58} \times 1000$$

$\Delta T_b = 0.358$ °C

Boiling point of solution = boiling point of pure solvent – Elevation of boiling point

= 99.725 + 0.358

= 100.083 °C

Example (12):

The freezing point of pure compere is 178.4 °C. Find the freezing point of a solutions containing 2g of a non-volatile compound, having molecular mass 140.0, in 40g of camphor. The molar freezing point content of camphor is 37.7 °C kg $mole^{-1}$.

Ans. **Given Data:**

Freezing point of camphor = 178.4 °C
Mass of solute = W_2 = 2.00g
Mass of solvent = W_1 = 40g
Molar Mass of solute = M_2 = 140g mol^{-1}
Molar freezing point constant of solvent = 37.7 °C kg mol^{-1}

Required:

Freezing point of solution = ?

Solution:

Formula:

$$\Delta T_f = K_f \frac{W_2}{W_1 \times M_2} \times 1000$$

We have to calculate, the freezing point of solution, so first we get the depression in freezing point ΔT_f then subtract it from freezing point of pure solvent

$$\Delta T_f = \frac{37.7 \times 2}{40 \times 140} \times 1000$$

$\Delta T_f = 13.46$ °C

Freezing point of solution = Freezing point of solvent – ΔT_f

= 178.4 °C – 13.46 = 164.94 °C

Freezing point of solution = **164.94 °C**

Additional Questions

Q. Explain why $CuSO_4$ give acidic solution, when dissolved in water?

Ans. The aqueous solution $CuSO_4$ is acidic in nature due to hydrolysis of $CuSO_4$ in water

When $CuSO_4$ is dissolved in water it hydrolyze to produce $Cu(OH)_2$ and H_2SO_4 in water as, follows

$$CuSO_{4(aq)} + H_2O_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2H^+_{(aq)} + SO_{4(aq)}^{-2}$$

$Cu(OH)_2$ is a weak base and does not ionize in water, while H_2SO_4 is a strong acid completely ionize in water to produce H^+ and SO_4^{-2} ions. Due to complete ionization of H_2SO_4, the concentration of H^+ ions in the solution increases and the solution become acidic in nature.

Q. Why a non-volatile solute in a volatile solvent lowers the vapour pressure of solution?

Ans. The vapour pressure of a liquid is decreased, when a non-volatile solute is dissolved in a volatile solvent due to following reasons.

(i) Due to presence of solute particles, the escaping tendency of solvent particles from the surface to the solution decreases and its vapor pressure is lowered.

(ii) Forces of attraction are produced between solute and solvent particles, which also hinders the evaporation of solvent molecules and its vapour pressure decreases.

Q. Give any two points which show the ideality of a solution.

Ans. When two liquid substances are mixed together, the solution formed may be ideal or non-ideal. A solution is called ideal, if it obeys the following conditions.

(i) If the forces of interactions between the molecules of different components are same as when they were in the pure state, the solution is ideal.

(ii) If the volume of the solution is equal to the sum of the individual volumes of the components, the solution is ideal.

Q. Differentiate between hydration and hydrolysis, with one example each.

Ans.

Hydration	Hydrolysis
(i) The process in which water molecules surround and interact with the solute ions is called as hydration.	(i) The reaction between the salt and the H^+ and OH^- ions of water to produce acid or base is called hydrolysis.
(ii) In hydration complete water molecules are physically attached with solute ions due to ion-dipole interactions.	(ii) In hydrolysis, the solute ions combine chemically with H^+ or OH^- ion of water to produce new compounds.
(iii) Hydration does not alter the pH of the solution. e.g., $Na^{+1}_{(aq)} + H_2O_{(l)} \rightarrow Na^{+1}_{(aq)}$	(iii) During hydrolysis, the pH of solution is usually altered. e.g., $CuSO_{4(aq)} + H_2O_{(l)} \rightarrow Cu(OH)_2 + H_2SO_4$

Q. Define hydration energy. On what factors do it depends.

Ans. **Hydration Energy:**

"The amount of heat evolved or absorbed when one mole of gaseous ions are dissolved in water to form an infinitely dilute solution is called hydration energy" e.g.,

$H^+_{(g)} + H_2O \rightarrow H^+_{(aq)}$ $\Delta H = -1075$ kJ mol^{-1}

Factors Affecting Hydration Energy

Generally the hydration energies of ions depend upon their charge densities

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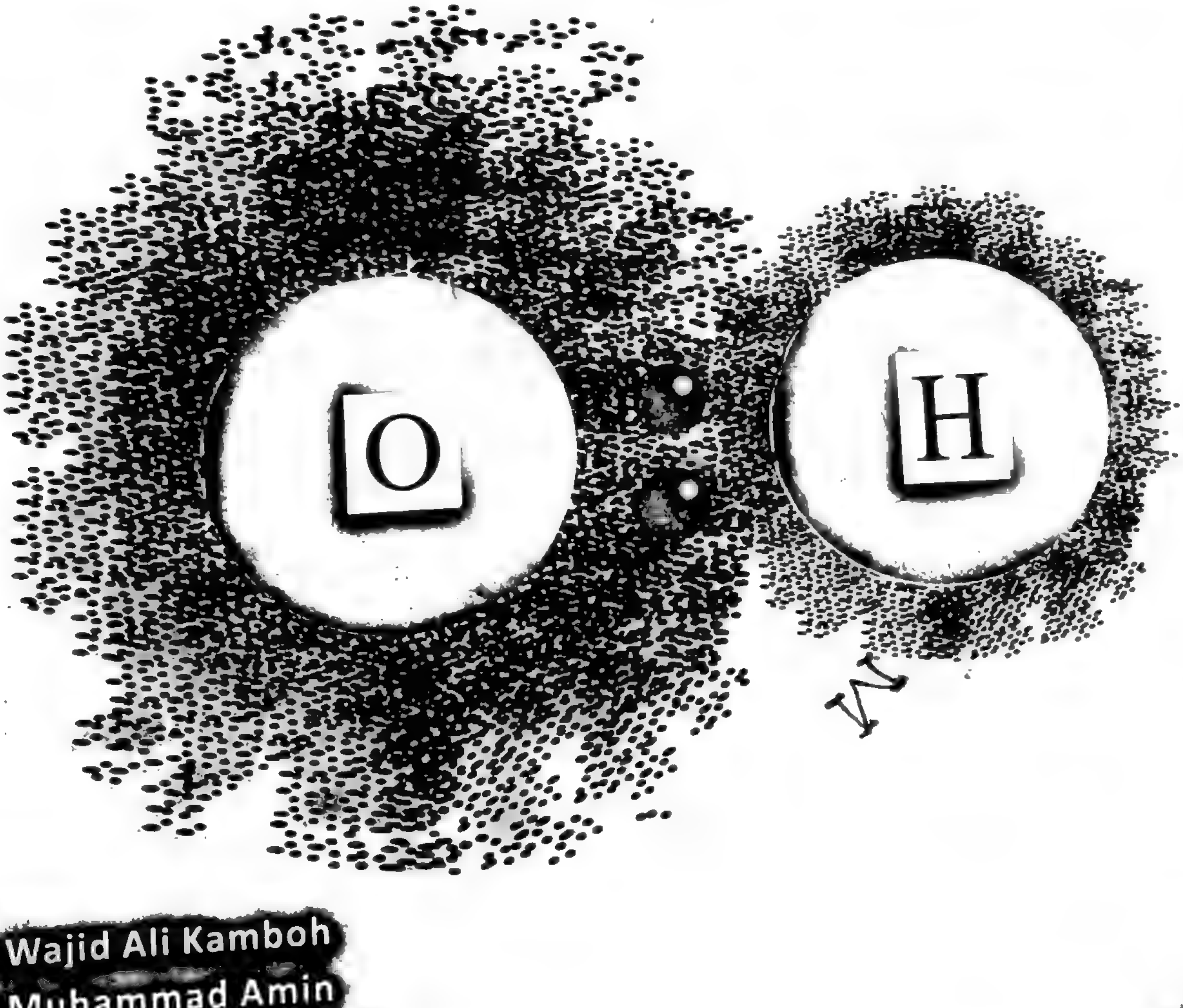

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Class 11

Chapter 1

BASIC CONCEPTS

HISTORICAL BACKGROUND OF ATOM

Greek philosophers

Greek philosophers thought that matter could be divided into smaller and smaller particles to reach a basic unit which could not be further sub-divided. **Democritus** named these smallest indivisible particles as atoms derived from "atomos" which means indivisible. These ideas of Greek philosophers were not based on experimental evidences.

17th Century work

In the late 17th century, the quantitative study of the composition of pure substances disclosed that a few elements were the components of many difficult substances. It was also investigated that how elements combined to form compounds and how compounds could be broken down into their constituent elements.

Dalton's atomic theory started chemistry on the road from a branch of philosophy to the science which it is today.

Dalton's work

In 1808, an English school teacher, John Dalton recognized that law of conservation of mass and law of definite proportions could only be explained by the existence of atoms. He developed a theory about atom called **Dalton's Atomic Theory**. The main postulate of atomic theory is that all matter is composed of atoms of different elements, which differ in their properties.

Element
A substance consisting of atoms which all have the same number of protons i.e. the same atomic number. Elements are chemically the simplest substances and hence cannot be broken down further using chemical methods. Elements can only be changed into other elements using nuclear methods.

Atom

The smallest particle of an element which can take part in a chemical reaction is called **atom**.

or

The smallest particle of an element which may or may not exist independently is called **atom**.

Examples

Atoms of **He, Ne, Ar, Kr, Xe** and **Rn** can exist independently while atoms of **H, O, N** etc. do not exist independently.

Sub-atomic particles

According to modern researches, atom is composed of sub-atomic particles like electron, proton, neutron, hypron, boson, neutrino, antineutrino etc. More than 100 such particles are thought to exist in an atom. However, electron, proton and neutron are regarded as fundamental particles of atoms.

J.Berzelius (Best experimental chemist) performed more than 2000 experiments over a 10 years period to determine atomic masses for 50 elements then known.

Berzelius's work

Swedish Chemist J. Berzelius (1779 – 1848) has following contribution in chemistry

- He determined the atomic masses of elements. A number of his values are close to the modern values of atomic masses.
- He developed the system of giving element a symbol.

$$\text{Charge density} = \frac{\text{Charge of ion}}{\text{Size of ion}}$$

Ions having high charge density have high values of hydration energies and vie versa.

Important Previous Board Questions

Q. Why a non-volatile solute in a volatile solvent lowers the vapour pressure of solution?
Q. What is positive deviation from Raoults Law?
Q. Heat of solution of a substance is measure at infinite dilution. Why?
Q. Freezing point of solvents are depressed due to presence of solutes. Justify.
Q. What are colligative properties? Why are they called so?
Q. Why aqueous solution of NH_4Cl is acidic but CH_3COONa is basic?
Q. When we plot a graph between temperature and compositions of binary liquid mixture, a straight line is not obtained. We get two curves even for ideal solutions. Justify it.
Q. Lower density of ice than water has got significance. Comment.
Q. Ethylene glycol may be used in the radiator of an automobile. Give two aspects of its use.
Q. What is meant by minimum boiling point mixture and maximum boiling point mixture?
Q. Why Beckmann's thermometer is used to note depression in freezing point?
Q. Give hydrolysis reactions of urea and glucose.

For Answers study Scholar's CHEMISTRY (Objective) XI

Chapter 10

ELECTROCHEMISTRY

ELECTROCHEMISTRY

"The branch of chemistry concerned with the conversion of electrical energy into chemical energy in electrolytic cells and chemical energy into electrical energy in galvanic or voltaic cells is called electrochemistry."

Differentiate between Electrolytic Cell and Voltaic Cell

Electrolytic cell	Voltaic/galvanic cell
• In this cell, electrical energy is converted into chemical energy.	• In this cell, the chemical energy is converted into electrical energy.
• Non-spontaneous redox reaction takes place.	• Spontaneous redox reaction takes place.
• Electrical energy is used to carry out reaction.	• Electrical energy is generated by a chemical reaction
• Electrolysis takes place.	• No electrolysis takes place.
• Anode is positive and cathode is negative.	• Anode is negative and cathode is positive.
• e.g. Down's cell (to prepare pure Na-metal), Nelson's cell (to prepare caustic soda commercially) etc.	• e.g. Zn-Cu cell (Daniel cell), lead storage battery, silver oxide cell etc

Q4. (a) Explain the term oxidation number with examples.

(b) Describe the rules used for the calculation of oxidation number of an element in molecules and ions giving examples.

Oxidation Number/Oxidation state

"The apparent charge on an atom of an element in a molecule or in an ion is called oxidation number or oxidation state."

Oxidation Number rules can be applied to any compound, whether ionic or covalent or ionic species.

Note: It may be zero, positive or negative.

Rules for assigning oxidation number

(i) The oxidation number of all elements in the free state is zero. This is often shown as a zero-written on the symbol.

e.g. $\overset{0}{H_2}, \overset{0}{Na}, \overset{0}{Mg}$ etc.

(ii) The oxidation number of an ion, consisting of a single element, is the same as the charge on the ion.

e.g. The oxidation number of $K^{+1}, Ca^{+2}, Al^{+3}, Br^{-1}, S^{-2}$ are +1, +2, +3, −1, −2 respectively.

(iii) The oxidation number of hydrogen in all its compounds except metal hydrides is +1. e.g. $CH_4^{+1}, H_2^{+1}O, H^{+1}Cl$ etc.

In metal hydrides it is −1. e.g. Na^+H^-, $Mg^{+2}H_2^{-1(2)}$

(iv) The oxidation number of oxygen in all its compounds except in peroxides, OF_2 and in super oxides is −2. It is −1 in peroxides and +2 in OF_2.

(v) In neutral molecules, the algebraic sum of the oxidation numbers of all the elements is zero.

(vi) In ions, the algebraic sum of oxidation number equals the charge on the ion.

(vii) In any substance, the more electronegative atom has the negative oxidation number.

Q4. (c) Calculate the oxidation number of Cr in the following compounds.

(i) $CrCl_3$

Ans. **Data:**

Oxidation Number of Cl = −1

Requirement:

Oxidation Number of Cr = x=?

Solution:

Oxidation Number of Gr + (O.S of Cl)3 = 0

$$x + 3(-1) = 0$$
$$x - 3 = 0$$
$$x = +3$$

Answer: Oxidation Number of Cr = +3 in $CrCl_3$.

(ii) $Cr_2(SO_4)_3$

Ans. **Data:**

Oxidation Number of O = −2

Oxidation Number of S = +6

Requirement:

Oxidation Number of Cr = x = ?

Solution:

2(Oxidation Number of Cr) + 3(O.S of S) + 12(O.S of O) = ?

$$2x + 3(+6) + 12(-2) = 0$$
$$2x + 18 - 24 = 0$$
$$2x = 24 - 18 = +6$$
$$x = +3$$

Answer: Oxidation Number of Cr is +3 in $Cr_2(SO_4)_3$.

(iii) K_2CrO_4

Ans. **Data:**

Oxidation Number of O = −2

Oxidation Number of K = +1

Requirement:

Oxidation Number of Cr = x = ?

Solution:

2(Oxidation Number of K) + (Oxidation Number of Cr) + 4(Oxidation Number of O) = 0

$$2(+1) + (x) + 4(-2) = 0$$
$$+2 + x - 8 = 0$$
$$x = +8 - 2 = +6$$

Answer: Oxidation Number of Cr = +6 in K_2CrO_4

(iv) $K_2Cr_2O_7$

Ans. **Data:**

Oxidation Number of O = −2

Oxidation Number of K = +1

Requirement:

Oxidation Number of Cr = x=?

Solution:

$$2(+1) + 2(x) + 7(-2) = 0$$
$$+2 + 2x - 14 = 0$$
$$2x = +14 - 2 = +12$$
$$x = +6$$

Answer: Oxidation Number of Cr is +6 in $K_2Cr_2O_7$.

(v) CrO_3

Ans. **Data:**

Oxidation Number of O = −2

Requirement:

Oxidation Number of Cr = x = ?

Solution:

(Oxidation Number of Cr) + 3(Oxidation Number of O) = 0

$$x + 3(-2) = 0$$
$$x - 6 = 0$$
$$x = +6$$

Answer: Oxidation Number of Cr is +6 in CrO_3.

(vi) Cr_2O_3

Ans. **Data:**

Oxidation Number of O = −2

Requirement:

Oxidation Number of Cr = x = ?

Solution:

2(Oxidation Number of Cr) + 3(Oxidation Number of O) = 0

$$2x + 3(-2) = 0$$
$$2x - 6 = 0$$
$$2x = +6$$
$$x = +3$$

Answer: Oxidation Number of Cr is +3 in Cr_2O_3.

(vii) $Cr_2O_7^{-2}$

Ans. **Data:**

Oxidation Number of O = −2

Requirement:

Oxidation Number of Cr : x = ?

Solution:

2(Oxidation Number of Cr) + 7(Oxidation Number of O) = −2

$$2x + 7(-2) = -2$$
$$2x - 14 = -2$$
$$2x = +14 - 2 = +12$$
$$x = +6$$

Answer: Oxidation Number of Cr is +6 in $Cr_2O_7^{-2}$.

Q4. (d) Calculate the oxidation number of elements underlined in the following compounds.

(i) $Ca(\underline{Cl}O_3)_2$

Ans. Data:

Oxidation Number of O = −2

Oxidation Number of Ca= +2

Requirement:

Oxidation Number of Cl = ? = x

Solution:

Oxidation Number of Ca + 2(Oxidation Number of Cl) + 6(Oxidation Number of O) = 0

$+2 + 2x + 6(-2) = 0$

$2x = +12 - 2 = +10$

$x = +5$

Answer: Oxidation Number of Cl is +5 in $Ca(ClO_3)_2$.

(ii) $Na_2\underline{C}O_3$

Ans. Data:

Oxidation Number of O = −2

Oxidation Number of Na = +1

Requirement:

Oxidation Number of C = x = ?

Solution:

2(Oxidation Number of Na) + (Oxidation Number of C) + 3(Oxidation Number of O) = 0

$2(+1) + (x) + 3(-2) = 0$

$2 + x - 6 = 0$

$x = +6 - 2 = +4$

Answer: Oxidation Number of C is +4 in Na_2CO_3.

(iii) $Na_3\underline{P}O_4$

Ans. Data:

Oxidation Number of O = −2

Oxidation Number of Na = +1

Requirement:

Oxidation Number of P = x = ?

Solution:

3(Oxidation Number of Na) + (Oxidation Number of P) + 4(Oxidation Number of O) = 0

$3(+1) + x + 4(-2) = 0$

$+3 + x - 8 = 0$

$x = +8 - 3 = +5$

Answer: Oxidation Number of P is +5 in Na_3PO_4.

(iv) $H\underline{N}O_3$

Ans. Data:

Oxidation Number of O = −2

Oxidation Number of H = +1

Requirement:

Oxidation Number of N = x = ?

Solution:

(Oxidation Number of H) + (Oxidation Number of N) + 3(Oxidation Number of O) = 0

$(+1) + x + 3(-2) = 0$

$+1 + x - 6 = 0$

$x = +6 - 1 = +5$

Answer: Oxidation Number of N is $\boxed{+5}$ in HNO_3.

(v) $Cr_2(\underline{S}O_4)_3$

Ans. Data:

Oxidation Number of O = −2

Oxidation Number of Cr= +3

Requirement:

Oxidation Number of S = x = ?

Solution:

2(Oxidation Number of Cr) + 3(Oxidation Number of S) + 12(Oxidation Number of O) = 0

$2(+3) + 3x + 12(-2) = 0$

$+6 + 3x - 24 = 0$

$3x = +24 - 6 = +18$

$x = +6$

Answer: Oxidation Number of S is +6 in $Cr_2(SO_4)_3$.

(vi) $H\underline{P}O_3$

Ans. Data:

Oxidation Number of O = −2

Oxidation Number of H = +1

Requirement:

Oxidation Number of P = x = ?

Solution:

(Oxidation Number of H) + (Oxidation Number of P) + 3(Oxidation Number of O) = 0

$+1 + x + 3(-2) = 0$

$+1 + x - 6 = 0$

$x = +6 - 1 = +5$

Answer: Oxidation Number of P is +5 in HPO_3.

(vii) $K_2\underline{Mn}O_4$

Ans. Data:

Oxidation Number of O = −2

Oxidation Number of K = +1

Requirement:

Oxidation Number of Mn = x = ?

Solution:

2(Oxidation Number of K) + (Oxidation Number of Mn) + 4(Oxidation Number of O) = 0

$2(+1) + x + 4(-2) = 0$

$2 + x - 8 = 0$

$x = +8 - 2 = +6$

Answer: Oxidation Number of Mn is +6 in K_2MnO_4.

Q5. (a) Describe the general rules for balancing a redox equation by oxidation number method.

Balancing of Redox Equations by Oxidation Number Method

Carry out the following steps for balancing of redox equations by oxidation number method.

(i) Write down the skeleton equation of the redox reaction under consideration.

(ii) Identify the elements, which undergo a change in their oxidation number during the reaction.

(iii) Record the oxidation number above the symbols of the element, which have undergone a change in the oxidation number.

(iv) Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation. It shows number of electrons gained or lost.

(v) Equate the increase or decrease in the oxidation number, i.e. electrons gained or lost by multiplying with a suitable digit.

(vi) Balance the rest of the equation by inspection method.

Q5. (b) Balance the following equations by oxi-number method.

(i) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

Ans.

(i) Write the equation with the oxidation number of each element.

$$\overset{0}{Cu} + \overset{+1}{H}\overset{+5}{N}\overset{(-2)3}{O_3} \rightarrow \overset{+2}{Cu}\overset{+10(-2)6}{(NO_3)_2} + \overset{+4}{N}\overset{(-2)2}{O_2} + \overset{(+1)2}{H_2}\overset{-2}{O}$$

(ii) Identify, those elements whose oxidation number have changed.

$$\overset{0}{Cu} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

(iii) Write HNO_3 twice on left hand side because N is present in two oxidation form on right hand side i.e. +5 and +4

$$HNO_3 + \overset{0}{Cu} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

(iv) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

Oxidation$(-2e^-)$

$$HNO_3 + \overset{0}{Cu} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

Reduction$(+1e^-)$

(v) Equate the increase or decrease in the oxidation number by multiplying with suitable digit.

Oxidation$(-2e^-)$

$$HNO_3 + \overset{0}{Cu} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

Reduction$(+1e^-)\times 2$

$$HNO_3 + Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

(vi) Balance the rest of the equation by inspection method.

$$2HNO_3 + Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

or

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(ii) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$

Ans.

(i) Write the equation with the oxidation number of each element.

$$\overset{0}{Zn} + \overset{+1}{H}\overset{+5}{N}\overset{(-2)3}{O_3} \rightarrow \overset{+2}{Zn}\overset{+10(-2)6}{(NO_3)_2} + \overset{+2}{N}\overset{-2}{O} + \overset{(+1)2}{H_2}\overset{-2}{O}$$

(ii) Identify, those elements whose oxidation number have changed.

$$\overset{0}{Zn} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

(iii) Write HNO_3 twice on left hand side because N is present in two oxidation form on right hand side i.e. +5 and +4

$$HNO_3 + \overset{0}{Zn} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

(iv) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

Oxidation$(-2e^-)$

$$HNO_3 + \overset{0}{Zn} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

Reduction$(+3e^-)$

(v) Equate the increase or decrease in the oxidation number by multiplying with suitable digit.

Oxidation$(-2e^-)\times 3$

$$HNO_3 + \overset{0}{Zn} + H\overset{+5}{N}O_3 \rightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

Reduction$(+3e^-)\times 2$

(vi) Write equation without arrows and without oxidation number.

$$HNO_3 + 3Zn + 2HNO_3 \rightarrow 3Zn(NO_3)_2 + 2NO + H_2O$$

(vii) Balance the rest of the equation by inspection method.

$$6HNO_3 + 3Zn + 2HNO_3 \rightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

or

$$3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

(iii) $Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$

Ans.

(i) Write the equation with the oxidation number of each element.

$$\overset{0}{Br_2} + \overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} \rightarrow \overset{+1}{Na}\overset{-1}{Br} + \overset{+1}{Na}\overset{+5}{Br}\overset{(-2)3}{O_3} + \overset{+2}{H_2}\overset{-2}{O}$$

(ii) Identify, those elements whose oxidation number have changed.

$$\overset{0}{Br_2} + NaOH \rightarrow Na\overset{-1}{Br} + Na\overset{+5}{Br}O_3 + H_2O$$

(iii) Write Br_2 twice on left hand side because Br is present in two oxidation form on right hand side i.e. -1 and +5

$$\overset{0}{Br_2} + \overset{0}{Br_2} + NaOH \rightarrow Na\overset{-1}{Br} + Na\overset{+5}{Br}O_3 + H_2O$$

(iv) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

$$\overset{0}{Br_2} + \overset{0}{Br_2} + NaOH \rightarrow 2Na\overset{-1}{Br} + 2Na\overset{+5}{Br}O_3 + H_2O$$

Reduction $(+2e^-)$; Oxidation $(-10e^-)$

(v) Equate the increase or decrease in the oxidation number by multiplying with suitable digit.

$$\overset{0}{Br_2} + \overset{0}{Br_2} + NaOH \rightarrow 2Na\overset{-1}{Br} + 2Na\overset{+5}{Br}O_3 + H_2O$$

Reduction $(+2e^-)\times 5$; Oxidation $(-10e^-)\times 1$

(vi) Write equation without arrows and without oxidation number.

$$Br_2 + 5Br_2 + NaOH \rightarrow 10NaBr + 2NaBrO_3 + H_2O$$

(vii) Balance the rest of the equation by inspection method.

$$Br_2 + 5Br_2 + 12NaOH \rightarrow 10NaBr + 2NaBrO_3 + 6H_2O$$

or

$$6Br_2 + 12NaOH \rightarrow 10NaBr + 2NaBrO_3 + 6H_2O$$

By simplifying it

$$3Br_2 + 6NaOH \rightarrow 5NaBr + NaBrO_3 + 3H_2O$$

(iv) $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

Ans.

(i) Write the equation with the oxidation number of each element.

$$\overset{+4}{Mn}\overset{(-2)2}{O_2} + \overset{+1}{H}\overset{-1}{Cl} \rightarrow \overset{+2}{Mn}\overset{(-1)2}{Cl_2} + \overset{+2}{H_2}\overset{-2}{O} + Cl_2^0$$

(ii) Identify, those elements whose oxidation number have changed.

$$\overset{+4}{Mn}O_2 + HC\overset{-1}{l} \rightarrow \overset{+2}{Mn}\overset{-1}{Cl_2} + H_2O + Cl_2^0$$

(iii) Write HCl twice on left hand side because Cl is present in two oxidation form on right hand side i.e. -1 and 0

$$2HCl + \overset{+4}{Mn}O_2 + 2HC\overset{-1}{l} \rightarrow \overset{+2}{Mn}Cl_2 + H_2O + Cl_2^0$$

(iv) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

Oxidation $(-2e^-)$

$$2HCl + \overset{+4}{Mn}O_2 + 2HC\overset{-1}{l} \rightarrow \overset{+2}{Mn}Cl_2 + H_2O + Cl_2^0$$

Reduction $(+2e^-)$

(v) Write equation without arrows and without oxidation number.

$$2HCl + MnO_2 + 2HCl \rightarrow MnCl_2 + H_2O + Cl_2$$

(vii) Balance the rest of the equation by inspection method.

$$2HCl + MnO_2 + 2HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

or

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

(v) $FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2O + Cr_2(SO_4)_3 + Fe_2(SO_4)_3$

Ans.

(i) Write the equation with the oxidation number of each element.

$$\overset{+2}{Fe}\overset{+6}{S}\overset{(-2)4}{O_4} + \overset{(+1)2}{K_2}\overset{+6}{Cr_2}\overset{(-2)4}{O_4} + \overset{+2}{H_2}\overset{+6\,-8}{SO_4} \rightarrow \overset{(+3)2}{Fe_2}\left(\overset{(+6)(-2)12}{SO_4}\right)_3 + \overset{(+3)2}{Cr}\left(\overset{+6(-2)12}{SO_4}\right)_3 + \overset{(+1)2\,+6\,-2}{K_2SO_4} + \overset{(+1)2\,-2}{H_2O}$$

(ii) Identify, those elements whose oxidation number have changed.

$$\overset{+2}{Fe}SO_4 + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \rightarrow \overset{(+3)2}{Fe_2}(SO_4)_3 + \overset{(+3)2}{Cr}(SO_4)_3 + K_2SO_4 + H_2O$$

(iii) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

Oxidation ( )

$$2\overset{+2}{Fe}SO_4 + K_2Cr_2O_7 + H_2SO_4 \rightarrow \overset{(+3)2}{Fe_2}(SO_4)_3 + \overset{(+3)2}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$$

Reduction $(+6e^-)$

(iv) Equate the increase or decrease in the oxidation number by multiplying with suitable digit.

Oxidation $(-2e^-)\times 3$

$$2\overset{+2}{Fe}SO_4 + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \rightarrow \overset{(+3)2}{Fe_2}(SO_4)_3 + \overset{(+3)2}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$$

Reduction $(+6e^-)\times 1$

(v) Write equation without arrows and without oxidation number.

$$6FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

(vi) Balance the rest of the equation by inspection method.

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

(vi) $HNO_3 + HI \longrightarrow NO + H_2O + I_2$

Ans.

(i) Write the equation with the oxidation number of each element.

$$\overset{+1\,+5\,(-2)3}{HNO_3} + \overset{+1\,-1}{HI} \rightarrow \overset{+2\,-2}{NO} + \overset{0}{I_2} + \overset{+2\,-2}{H_2O}$$

(ii) Identify, those elements whose oxidation number have changed.

$$H\overset{+5}{N}O_3 + H\overset{-1}{I} \rightarrow \overset{+2}{N}O + \overset{0}{I_2} + H_2\overset{-2}{O}$$

(iii) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

Oxidation $(-2e^-)$

$$H\overset{+5}{N}O_3 + 2H\overset{-1}{I} \rightarrow \overset{+2}{N}O + \overset{0}{I_2} + H_2\overset{-2}{O}$$

Reduction $(+3e^-)$

(iii) Equate the increase or decrease in the oxidation number by multiplying with suitable digit

$$HNO_3 + 2HI \rightarrow \overset{+2}{N}O + I_2 + H_2\overset{-2}{O}$$

(iv) Write equation without arrows and without oxidation number.

$$2HNO_3 + 6HI \rightarrow 2NO + 3I_2 + H_2O$$

(v) Balance the rest of the equation by inspection method.

$$2HNO_3 + 6HI \rightarrow 2NO + 3I_2 + 4H_2O$$

(vii) $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

Ans.

(i) Write the equation with the oxidation number of each element.

$$\overset{0}{Cu} + \overset{(+1)2}{H_2}\overset{+6}{S}\overset{(-2)4}{O_4} \rightarrow \overset{+2}{Cu}\overset{+6}{S}\overset{(-2)4}{O_4} + \overset{+4}{S}\overset{(-2)2}{O_2} + \overset{(+1)2}{H_2}\overset{-2}{O}$$

(ii) Identify, those elements whose oxidation number have changed.

$$\overset{0}{Cu} + H_2\overset{+6}{S}O_4 \rightarrow \overset{+2}{Cu}\overset{+6}{S}O_4 + \overset{+4}{S}O_2 + H_2O$$

(iii) Write H_2SO_4 twice on left hand side because S is present in two oxidation form on right hand side i.e. +6 and +4

$$H_2SO_4 + \overset{0}{Cu} + H_2\overset{+6}{S}O_4 \rightarrow \overset{+2}{Cu}\overset{+6}{S}O_4 + \overset{+4}{S}O_2 + H_2O$$

(iv) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

Oxidation $(-2e^-)$

$$H_2SO_4 + \overset{0}{Cu} + H_2\overset{+6}{S}O_4 \rightarrow \overset{+2}{Cu}\overset{+6}{S}O_4 + \overset{+4}{S}O_2 + H_2O$$

Reduction $(+2e^-)$

(v) Write equation without arrows and without oxidation number.

$$H_2SO_4 + Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$$

(vi) Balance the rest of the equation by inspection method.

$$H_2SO_4 + Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

or

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

(viii) $HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$

Ans.

(i) Write the equation with the oxidation number of each element.

$$\overset{+1}{H}\overset{-1}{I} + \overset{(+1)2}{H_2}\overset{+6}{S}\overset{(-2)4}{O_4} \rightarrow \overset{0}{I_2} + \overset{+4}{S}\overset{(-2)2}{O_2} + \overset{(+1)2}{H_2}\overset{-2}{O}$$

(ii) Identify, those elements whose oxidation number have changed.

$$H\overset{-1}{I} + H_2\overset{+6}{S}O_4 \rightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + H_2O$$

(iii) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

Oxidation $(-2e^-)$

$$2H\overset{-1}{I} + H_2\overset{+6}{S}O_4 \rightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + H_2O$$

Reduction $(+2e^-)$

(iv) Write equation without arrows and without oxidation number

$$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + H_2O$$

(v) Balance the rest of the equation by inspection method

$$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$$

(ix) $NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + Cl_2 + H_2O$

Ans.

(i) Write the equation with the oxidation number of each element

$$\overset{+1}{Na}\overset{-1}{Cl} + \overset{(+1)2}{H_2}\overset{+6}{S}\overset{(-2)4}{O_4} + \overset{+4}{Mn}\overset{(-2)2}{O_2} \rightarrow \overset{(+1)2}{Na_2}\overset{+6}{S}\overset{(-2)4}{O_4} + \overset{+2}{Mn}\overset{+6}{S}\overset{(-2)4}{O_4} + \overset{0}{Cl_2} + \overset{(+1)2}{H_2}\overset{-2}{O}$$

(ii) Identify, those elements whose oxidation number have changed

$$Na\overset{-1}{Cl} + H_2SO_4 + \overset{+4}{Mn}O_2 \rightarrow Na_2SO_4 + \overset{+2}{Mn}SO_4 + \overset{0}{Cl_2} + H_2O$$

(iii) Draw the arrows between the same elements whose oxidation number have changed and mention number of electron gain or lost

Oxidation $(-2e^-)$

$$2Na\overset{-1}{Cl} + H_2SO_4 + \overset{+4}{Mn}O_2 \rightarrow Na_2SO_4 + \overset{+2}{Mn}SO_4 + \overset{0}{Cl_2} + H_2O$$

Reduction $(+2e^-)$

(iv) Write equation without arrows and without oxidation number

$$2NaCl + H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + Cl_2 + H_2O$$

(v) Balance the rest of the equation by inspection method.

$$2NaCl + 2H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + Cl_2 + 2H_2O$$

Q6. (a) Describe the general rules for balancing a redox equation by ion-electron method.

Balancing of Redox Equation by Ion-Electron Method

The balancing of redox equations by the loss and gain of electrons, usually involves quite a few ions, which do not undergo change in valence and which are not really necessary for the process of balancing. The ion-electron method eliminates all the unnecessary ions and retains only those, which are essential. Following, are the general rules for balancing the redox equations by ion-electron method

1. Write a skelton equation that shows only those substances that are actually involved in the reaction
2. Split the equation into two half reactions, one showing oxidation half reaction and the other reduction half reaction.

3. The element should not be written as a free atom or ion unless it really exists as such. It should be written as a real molecular or ionic species.
4. Balance each partial equation as to the number of atoms of each element. In neutral or acidic solution, H_2O or H^+ ions may be added for balancing oxygen and hydrogen atoms. Oxygen atoms are balanced first. If the solution is alkaline, OH^- may be used for each excess oxygen on one side of the equation.
5. Balance each half reaction as to the number of charges by adding electrons to either the left or the right side of the equation.
6. Multiply each half reaction by a number chosen so that the total number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent.
7. Add the two half reactions. Count the number of atoms of each element on each side of the equation and also check the net charge on each side, which should be equal on both sides.

Q6. (b) Balance the following equations by ion-electron method.

(i) $Fe^{+3} + Sn^{+2} \longrightarrow Fe^{+2} + Sn^{+4}$

Ans.

(i) Split the reaction into two half reactions.

Oxidation-half reaction

$$Sn^{+2} \longrightarrow Sn^{+4}$$

Reduction-half reaction

$$Fe^{+3} \longrightarrow Fe^{+2}$$

(ii) Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side.

$$Sn^{+2} \longrightarrow Sn^{+4} + 2e^-$$
$$1e^- + Fe^{+3} \longrightarrow Fe^{+2}$$

(iii) Multiply each half reaction by an appropriate number so that the number of electrons on both side of the half reaction becomes equal. For this purpose, multiply the oxidation half reaction by 1 and the reduction half reaction by 2

$$(Sn^{+2} \longrightarrow Sn^{+4} + 2e^-)\times 1$$
$$(1e^- + Fe^{+3} \longrightarrow Fe^{+2})\times 2$$

(iv) Add the two half reactions to get the net ionic equation and cancel out anything appearing on both sides of the equations.

$$Sn^{+2} \longrightarrow Sn^{+4} + 2e^-$$
$$\underline{2e^- + 2Fe^{+3} \longrightarrow 2Fe^{+2}}$$
$$2Fe^{+3} + Sn^{+2} \longrightarrow 2Fe^{+2} + Sn^{+4}$$

(ii) $MnO_4^- + C_2O_4^{-2} \longrightarrow Mn^{+2} + CO_2$

Ans.

(i) Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.

$$\left[\overset{+7}{Mn}\overset{(-2)4}{O_4}\right]^{-1} + \left[\overset{(3)2}{C_2}\overset{(-2)4}{O_4}\right]^{2-} \rightarrow \overset{2+}{Mn} + \overset{+4}{C}\overset{(-2)2}{O_2}$$

The elements undergoing change in oxidations number are Mn and C.

(ii) Split the reaction into two half reactions.

Oxidations half reaction

$$C_2O_4^{2-} \longrightarrow CO_2$$

Reduction half reaction

$$MnO_4^{-1} \longrightarrow Mn^{+2}$$

(iii) Balancing the atoms on both sides of oxidation and reduction half reactions by using H^+ and H_2O

$$C_2O_4^{2-} \longrightarrow 2CO_2$$
$$MnO_4^{-1} + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$$

(iv) Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$
$$5e^- + MnO_4^{-1} + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$$

(v) Multiply each half reaction by an appropriate number, so that the number of electrons on both side of the half reaction becomes equal. For this purpose, multiply the oxidation half reaction by 5 and the reduction half reaction by 2.

$$(C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-)\times 5$$
$$(5e^- + MnO_4^{-1} + 8H^+ \longrightarrow Mn^{+2} + 4H_2O)\times 2$$

(vi) Add the two half reactions to get the net ionic equation and cancel out anything appearing on both sides of the equation.

$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$$
$$\underline{10e^- + 2MnO_4^{-1} + 16H^+ \longrightarrow 2Mn^{+2} + 8H_2O}$$
$$2MnO_4^{-1} + 5C_2O_4^{2-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$$

(iii) $Cr_2O_7^{-2} + Fe^{+2} \longrightarrow Fe^{+3} + Cr^{+3}$

Ans.

(i) Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.

$$\left[\overset{(+6)2}{Cr_2}\overset{(-2)7}{O_7}\right]^{2-} + Fe^{2+} \rightarrow Fe^{3+} + Cr^{3+}$$

(ii) Split the reaction into two half reactions.

Oxidations half reaction

$$Fe^{2+} \rightarrow Fe^{3+}$$

Reduction half reaction

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{+3}$$

(iii) Balancing the atoms on both sides of oxidation and reduction half reactions by using H^+ and H_2O

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{+3} + 7H_2O$$

(iv) Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O$$

(v) Multiply each half reaction by an appropriate number, so that the number of electrons on both side of the half reactions becomes equl. For this purpose, multiply the oxidation half reaction by 6 and the reduction half reaction by 1

$$(Fe^{2+} \rightarrow Fe^{3+} + 1e^-)\times 6$$

$(Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O) \times 1$

(vi) Add the two half reactions to get the net ionic equation and cancel out anything appearing on both sides of the equation

$6Fe^{+2} \rightarrow 6Fe^{+3} + 6e$

$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{+3} + 7H_2O$

$Cr_2O_7^{2-} + 6Fe^{+2} + 14H^+ \longrightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O$

(iv) $Cr_2O_7^{-2} + Cl^- \longrightarrow Cr^{+3} + Cl_2$

Ans.

(i) Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.

$$\left[\overset{(+6)2(-2)7}{Cr_2\,O_7}\right]^{-2} + Cl \rightarrow Cr^{3+} + \overset{0}{Cl_2}$$

(ii) Split the reaction into two half reactions.

Oxidations half reaction

$Cl^- \rightarrow \overset{0}{Cl_2}$

Reduction half reaction

$Cr_2O_7^{2-} \longrightarrow 2Cr^{+3}$

(iii) Balancing the atoms on both sides of oxidation and reduction half reactions by using H^+ and H_2O

$2Cl^- \rightarrow \overset{0}{Cl_2}$

$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{+3} + 7H_2O$

(iv) Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side

$2Cl^- \rightarrow \overset{0}{Cl_2} + 2e$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O$

(v) Multiply each half reaction by an appropriate number, so that the number of electrons on both side of the half reactions becomes equl. For this purpose, multiply the oxidation half reaction by 3 and the reduction half reaction by 1

$(2Cl \rightarrow \overset{0}{Cl_2} + 2e) \times 3$

$(Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{+3} + 7H_2O) \times 1$

(vi) Add the two half reaction to get the net ionic equation and cancel out anything appearing on both sides of the equation

$6Cl^- \rightarrow 3\overset{0}{Cl_2} + 6e$

$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{+3} + 7H_2O$

$Cr_2O_7^{2-} + 6Cl + 14H^+ \longrightarrow 2Cr^{+3} + 3Cl_2 + 7H_2O$

(v) $Cu + NO_3^{-1} \longrightarrow Cu^{+2} + NO_2$

Ans.

(i) Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.

$$\overset{0}{Cu} + \left[\overset{+1(-2)3}{N\,O_3}\right]^{-1} \rightarrow Cu^{+2} + \overset{+4(-2)2}{NO_2}$$

(ii) Split the reaction into two half reactions.

Oxidations half reactions

$\overset{0}{Cu} \rightarrow Cu^{+2}$

Reduction half reactions

$NO_3^{-1} \longrightarrow NO_2$

(iii) Balancing the atoms on both sides of oxidation and reduction half reactions by using H^+ and H_2O

$NO_3^{-1} + 2H^+ \longrightarrow NO_2 + H_2O$

(iv) Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side

$\overset{0}{Cu} \rightarrow Cu^{+2} + 2e^-$

$NO_3^{-1} + 2H^+ + 1e^- \longrightarrow NO_2 + H_2O$

(v) Multiply each half reaction by an appropriate number, so that the number of electrons on both side of the half reactions becomes equal. For this purpose, multiply the oxidation half reaction by 1 and the reduction half reaction by 2

$(\overset{0}{Cu} \rightarrow Cu^{+2} + 2e^-) \times 1$

$(NO_3^{-1} + 2H^+ + 1e^- \longrightarrow NO_2 + H_2O) \times 2$

(vi) Add the two half reaction to get the net ionic equation and cancel out anything appearing on both sides of the equation

$\overset{0}{Cu} \rightarrow Cu^{+2} + 2e^-$

$2NO_3^{-1} + 4H^+ + e^- \longrightarrow 2NO_2 + 2H_2O$

$Cu + NO_3^{-1} + 4H^+ \longrightarrow Cu^{+2} + NO_2 + 2H_2O$

(vi) $S_2O_3^{-2} + OCl^{-1} \rightarrow S_4O_6^{-2} + Cl^{-1}$

Ans.

(i) Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.

$$\left[\overset{+4}{S_2}\,\overset{(-2)3}{O_3}\right]^{-2} + \left[\overset{-2\ +1}{OCl}\right]^{-1} \rightarrow \left[\overset{+10(-2)6}{S_4\,O_6}\right]^{-2} + Cl^-$$

(ii) Split the reaction into two half reactions.

Oxidations half reactions

$S_2O_3^{-2} \rightarrow S_4O_6^{-2}$

Reduction half reactions

$OCl^- \rightarrow Cl^{-1}$

(iii) Balancing the atoms on both sides of oxidation and reduction half reactions by using H^+ and H_2O

$2S_2O_3^{-2} \rightarrow S_4O_6^{-2}$

$OCl^- + 2H^+ \rightarrow Cl^{-1} + H_2O$

(iv) **Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side**

$$2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2e^-$$

$$OCl^- + 2H^+ + 2e^- \rightarrow Cl^{-1} + H_2O$$

(v) **Add the two half reaction to get the net ionic equation and cancel out anything appearing on both sides of the equation**

$$2S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2e^-$$

$$OCl^- + 2H^+ + 2e^- \rightarrow Cl^{-1} + H_2O$$

$$2S_2O_3^{-2} + OCl^- + 2H^+ \rightarrow S_4O_6^{-2} + Cl^{-1} + H_2O$$

(vii) $IO_3^{-1} + AsO_3^{-3} \rightarrow AsO_4^{-3} + I^{-1}$

Ans.

(i) **Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.**

$$\left[\overset{+5}{I}\overset{(-2)3}{O_3}\right]^{-1} + \left[\overset{+3}{As}\overset{(-2)3}{O_3}\right]^{-3} \rightarrow I^- + \left[\overset{+5}{As}\overset{(-2)4}{O_4}\right]^{-3}$$

(ii) **Split the reaction into two half reactions.**

Oxidations half reactions

$$AsO_3^{-3} \rightarrow AsO_4^{-3}$$

Reduction half reactions

$$IO_3^{-1} \rightarrow I^{-1}$$

(iii) **Balancing the atoms on both sides of oxidation and reduction half reactions by using H^+ and H_2O**

$$AsO_3^{-3} + H_2O \rightarrow AsO_4^{-3} + 2H^+$$

$$IO_3^{-1} + 6H^+ \rightarrow I^{-1} + 3H_2O$$

(iv) **Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side**

$$AsO_3^{-3} + H_2O \rightarrow AsO_4^{-3} + 2H^+ + 2e^-$$

$$IO_3^{-1} + 6H^+ + 6e^- \rightarrow I^{-1} + 3H_2O$$

(v) **Multiply each half reaction by an appropriate number, so that the number of electrons on both side of the half reactions becomes equal. For this purpose, multiply the oxidation half reaction by 3 and the reduction half reaction by 1**

$$\left(AsO_3^{-3} + H_2O \rightarrow AsO_4^{-3} + 2H^+ + 2e^-\right) \times 3$$

$$\left(IO_3^{-1} + 6H^+ + 6e^- \rightarrow I^{-1} + 3H_2O\right) \times 1$$

(vi) **Add the two half reaction to get the net ionic equation and cancel out anything appearing on both sides of the equation**

$$3AsO_3^{-3} + 3H_2O \rightarrow 3AsO_4^{-3} + 6H^+ + 6e^-$$

$$IO_3^{-1} + 6H^+ + 6e^- \rightarrow I^{-1} + 3H_2O$$

$$3AsO_3^{-3} + IO_3^{-1} \rightarrow 3AsO_4^{-3} + I^{-1}$$

(viii) $Cr^{3+} + BiO_3^{1-} \rightarrow Cr_2O_7^{2-} + 3Bi^{3+}$

Ans.

(i) Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.

$$Cr^{+3} + \left[\overset{+5}{Bi}\overset{(-2)3}{O_3}\right]^{1-} \rightarrow \left[\overset{+12}{Cr_2}\overset{(-2)7}{O_7}\right]^{-2} + 3Bi^{+3}$$

(ii) Split the reaction into two half reactions.

Oxidations half reactions

$$Cr^{+3} \rightarrow Cr_2O_7^{-2}$$

Reduction half reactions

$$BiO_3^{-1} \rightarrow 3Bi^{+3}$$

(iii) Balancing the atoms on both sides of oxidation and reduction half reactions by using H^+ and H_2O

$$2Cr^{+3} + 7H_2O \rightarrow Cr_2O_7^{-2} + 14H^+$$

$$3BiO_3^{-1} + 18H^+ \rightarrow 3Bi^{+3} + 9H_2O$$

(iv) Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side

$$2Cr^{+3} + 7H_2O \rightarrow Cr_2O_7^{-2} + 14H^+ + 6e^-$$

$$3BiO_3^{-1} + 18H^+ + 6e^- \rightarrow 3Bi^{+3} + 9H_2O$$

(v) Add the two half reaction to get the net ionic equation and cancel out anything appearing on both sides of the equation

$$2Cr^{+3} + 7H_2O \rightarrow Cr_2O_7^{-2} + 14H^+ + 6e^-$$

$$3BiO_3^{-1} + 18H^+ + 6e^- \rightarrow 3Bi^{+3} + 9H_2O$$

$$2Cr^{+3} + 3BiO_3^{-1} + 4H^+ \rightarrow Cr_2O_7^{-2} + 3Bi^{+3} + 2H_2O$$

(ix) $H_3AsO_3 + Cr_2O_7^{-2} \rightarrow 3H_3AsO_4 + 2Cr^{+3}$

Ans.

(i) Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.

$$\overset{(+1)3}{H_3}\overset{+3}{As}\overset{(-2)3}{O_3} + \left[\overset{+12}{Cr_2}\overset{(-2)7}{O_7}\right]^{-2} \rightarrow 3\overset{(+1)3}{H_3}\overset{+5}{As}\overset{(-2)4}{O_4} + 2Cr^{+3}$$

(ii) Split the reaction into two half reactions.

Oxidations half reactions

$$H_3AsO_3 \rightarrow 3H_3AsO_4$$

Reduction half reactions

$$Cr_2O_7^{-2} \rightarrow 2Cr^{+3}$$

(iii) Balancing the atoms on both sides of oxidation and reduction half reactions by using H^+ and H_2O

$$3H_3AsO_3 + H_2O \rightarrow 3H_3AsO_4 + 2H^+$$

$$Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$$

(iv) Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side

$$3H_3AsO_3 + H_2O \rightarrow 3H_3AsO_4 + 2H^+ + 2e$$

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$

(v) Multiply each half reaction by an appropriate number, so that the number of electrons on both side of the half reactions becomes equal. For this purpose, multiply the oxidation half reaction by 3 and the reduction half reaction by 1

$$\left(3H_3AsO_3 + H_2O \rightarrow 3H_3AsO_4 + 2H^+ + 2e^-\right)\times 3$$

$$\left(Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O\right)\times 1$$

(vi) Add the two half reaction to get the net ionic equation and cancel out anything appearing on both sides of the equation

$$9H_3AsO_3 + 3H_2O \rightarrow 9H_3AsO_4 + 6H^+ + 6e^-$$

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$$

$$9H_3AsO_3 + Cr_2O_7^{-2} + 8H^+ \rightarrow 9H_3AsO_4 + 2Cr^{+3} + 4H_2O$$

(x) $CN^- + MnO_4^{-1} \rightarrow CNO^- + MnO_2$ (Basic Medium)

Ans.

(i) Identify those elements, which undergo change in oxidation number by writing their oxidation number above each element.

$$\left[\overset{+2}{C}\overset{-3}{N}\right]^{-1} + \left[\overset{+7}{Mn}\overset{(-2)4}{O_4}\right]^{-1} \rightarrow \left[\overset{+4}{C}\overset{-5}{N}\overset{-2}{O}\right]^{-1} + \overset{+4}{Mn}\overset{(-2)2}{O_2}$$

(ii) Split the reaction into two half reactions.

Oxidations half reactions

$$CN^- \rightarrow CNO$$

Reduction half reactions

$$MnO_4^{-1} \rightarrow MnO_2$$

(iii) Balancing the atoms on both sides of oxidation and reduction half reactions by using OH^- and H_2O

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O$$

$$MnO_4^{-1} + 2H_2O \rightarrow MnO_2 + 4OH^-$$

(iv) Balancing the charges on both sides of the half reactions by adding the appropriate number of electrons to the more positive side

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^-$$

$$MnO_4^{-1} + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

(v) Multiply each half reaction by an appropriate number, so that the number of electrons on both side of the half reactions becomes equal. For this purpose, multiply the oxidation half reaction by 3 and the reduction half reaction by 2

$$\left(CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^-\right)\times 3$$

$$\left(MnO_4^{-1} + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-\right)\times 2$$

(vi) Add the two half reaction to get the net ionic equation and cancel out anything appearing on both sides of the equation

$$3CN^- + 6OH^- \rightarrow 3CNO^- + 3H_2O + 6e$$

$$2MnO_4^{-1} + 4H_2O + 6e^- \rightarrow 2MnO_2 + 8OH^-$$

$$3CN^- + 2MnO_4^{-1} + H_2O \rightarrow 3CNO^- + 2MnO_2 + 2OH$$

Conductor

The substances which allow electric current to pass through them are called conductors.

Conductors are of two types:

(1) Metallic conductors

(2) Electrolytes

Metallic conductors

These are the metals through which electricity can pass and no chemical change takes place e.g., Cu, Ag, Al etc

Metallic conduction

Most metals are conductors of electricity because of the relatively free movement of their electrons throughout the metallic lattice. This electronic conduction is simply called metallic conduction.

Electrolytic conduction

Conduction that takes place due to mobile ions of an electrolyte during electrolysis is called electrolytic conduction.

Electrolytes

The substances which allow electric current to pass through them in molten state or in the form of their aqueous solutions and at the same time undergo chemical decomposition are called electrolytes.

In electrolytes, the current is not carried by the free electrons. Here the current is carried by positive and negative ions which are produced due to ionization of electrolyte.

Ionization is the process in which ionic compounds when fused or dissolved in water split up into charged particles called ions.

$$PbBr_{2(s)} \xrightleftharpoons{H_2O} Pb^{2+}_{(aq)} + 2Br^-_{(aq)}$$

$$NaCl_{(s)} \xrightleftharpoons{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$$

Electrolysis

When a non-spontaneous reaction take place at the expense of electrical energy, the process is called electrolysis. During this non-spontaneous reaction, the substances are deposited at respective electrodes and electrolyte is decomposed.

Q12. (a) Explain the differences between Ionization and electrolysis.

Ans.

Ionization	Electrolysis
(i) When ionic compounds or electrolytes dissolve in water or in molten state, they split up into ions. The process is called ionization.	(i) The Electrochemical reactions that occur at electrodes during the electrolytic conduction is called electrolysis (a non-spontaneous redox reaction)
(ii) An ordinary apparatus for example beaker, flask etc. can be used for this process.	(ii) A specially devised electrolytic cell is used to carry out electrolysis
(iii) Ions are the product of ionization.	(iii) During electrolysis, the ions of electrolyte go to respective electrode and undergo redox reactions
Examples:- ionization of NaCl is $NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$	Electrolysis of NaCl (molten) $NaCl_{(l)} \rightleftharpoons Na^+_{(l)} + Cl^-_{(l)}$ At anode $2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e$

Ans.

Ionization	Electrolysis
	At cathode : $2Na^+_{(l)} + 2e^- \rightarrow 2Na_{(s)}$ Overall : $2Na^+_{(l)} + 2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2Na_{(s)}$ reaction

Q12. (c) Explain the difference between conduction through metals and molten electrolytes.

Ans.

Metallic or electronic conduction	Electrolytic conduction
(i) Conduction that takes place due to mobile electron of metals is metallic or electronic conduction.	(i) Conduction that takes place due to mobile ions of an electrolyte during electrolysis is called electrolytic conduction.
(ii) Conduction is possible when metals are in solid state.	(ii) For electrolytic conduction electrolyte is either in molten or liquid state.
(iii) No appreciable change in physical or chemical properties of metal occurs during metallic conduction.	(iii) During electrolytic conduction, the ions undergo reduction or oxidation at respective electrodes
(iv) This type of conduction decreases with increase in temperature.	(iv) In electrolytic conduction the conduction increases with increase in temperature.
(v) For example, conduction of electricity through Cu-wire.	(v) The Conduction of current through $CuSO_4$ solution results in a redox reaction at electrodes.

ELECTROCHEMICAL CELL

A cell in which electrical energy is used to bring about a redox reaction or electrical energy is produced by a redox reaction is called electrochemical cell.

Electrochemical cells are of two types:

1. Electrolytic cell
2. Galvanic or voltaic cell

ELECTROLYTIC CELL

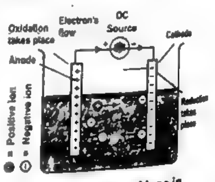
An electrochemical cell in which electric current is used to bring about a non-spontaneous redox reaction is called electrolytic cell. e.g., Down's cell, Nelson's cell etc.

Electrolytic conduction

"The movement of ionic charges through the liquid brought by the application of electricity is called electrolytic conduction."

Construction of electrolytic cell

The electrolyte is consisted of positive and negative ions which are free to move in the solution. When a direct current (D.C.) source is connected to the electrodes of the cell containing positive and negatively charged ions of the electrolyte, each electrode acquires an electric charge. Thus, when an electric potential is applied, the positive ions migrate towards the negatively charged electrode called cathode and the negative ions move towards the positive electrode called anode.



The migration of ions in electrolytic cell

Working

When electrolytic conduction occurs electrochemical reactions takes place. The ions in the liquid come in contact with the electrodes.

At the anode, the negative ions give up electrons and are, therefore, oxidized.

At the cathode, the positive ions pick up electrons and are reduced. Thus during electrolytic conduction, reduction takes place at cathode.

Note

- The liquid will continue to conduct electricity only as long as oxidation-reduction reactions, occurring at the electrodes, continue.
- When molten salt is electrolyzed the products are predictable
- When an aqueous solution of a salt is electrolyzed, hydrogen and oxygen appear at the cathode and anode, respectively in certain cases.

Products of Electrolysis

(a) Using inert electrodes (platinum or graphite)

Electrolyte	Cathode	Anode
$PbBr_{2(molten)}$	$Pb_{(l)}$	$Br_{2(g)}$
$NaCl_{(molten)}$	$Na_{(s)}$	$Cl_{2(g)}$
$NaCl_{(aq)}$	$H_{2(g)}$	$Cl_{2(g)}$
$CuCl_{2(aq)}$	$Cu_{(s)}$	$Cl_{2(g)}$
$CuSO_{4(aq)}$	$Cu_{(s)}$	$O_{2(g)}$
$KNO_{3(aq)}$	$H_{2(g)}$	$O_{2(g)}$
$NaOH_{(aq)}$	$H_{2(g)}$	$O_{2(g)}$
$H_2SO_{4(aq)}$	$H_{2(g)}$	$O_{2(g)}$

(b) When electrodes take part in the reaction

Electrolyte	Copper cathode	Copper anode
$CuSO_{4(aq)}$	Cu deposits	$Cu_{(s)}$ dissolves to form Cu^{2+} ions
Electrolyte	**Silver Cathode**	**Silver anode**
$AgNO_{3(aq)}$ and $HNO_{3(aq)}$	Ag deposits	$Ag_{(s)}$ dissolves to form Ag^+ ions

Q8. Outline the important applications of electrolysis. Write the electrochemical reactions involved therein. Discuss the electrolysis of $CuSO_4$ using Cu-electrodes and $AgNO_3$ solution using Ag electrode.

Ans. **(a) Electrolysis of $AgNO_3$ using Ag electrodes:**

The electrolytic cell is briefly described as

Cathode = Ag-metal (pure)

Anode = Ag-metal (impure)

Electrolyte = $AgNO_3 \rightleftharpoons Ag^{+1} + NO_3^{-1}$

Reactions at electrodes are

At anode: $Ag^0 \rightarrow Ag^{+1} + 1e^-$
$Ag^{+1} + NO_3^- \rightarrow AgNO_3$ (oxidation)

at cathode: $Ag^+ + 1e^- \rightarrow Ag^0$ (reduction)

Ag^+ dissolves from impure electrode in solution then goes to cathode where it is deposited as pure Ag-metal.

Impurities are left at anode or as a mud in electrolyte.

(b) Electrolysis of $CuSO_4$ using Cu-electrodes

The electrolytic cell is briefly described as

Cathode = Cu-metal (pure)

Anode = Cu-metal (impure)

Electrolyte $= CuSO_4 \rightleftharpoons Cu^{+2}_{(aq)} + SO_{4(aq)}^{-2}$

Reactions at electrodes are

At anode: $Cu_{(s)} \rightarrow Cu^{+2}_{(aq)} + 2e^-$

At cathode: $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

The copper ions (Cu^{+2}) dissolve in solution from impure copper electrode goes to the cathode gain electrons and deposit on pure copper metal.

Impurities are left at anode as a mud in electrolyte.

Explanation of Electrolysis

(a) Electrolysis of Fused Salts

When electric current is passed through a fused salt (molten salt), the metal cations move towards cathode, gain electrons and are reduced to metal. The anions move towards anode, give up their electrons to the anode and are oxidized

Example

When electric current is passed through molten $PbCl_2$, following changes occur at the electrodes.

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{1-}_{(aq)}$$

At cathode Pb^{+2} ions gain electrons and are reduced to metallic Pb.

$$Pb^{+2}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$$

At anode Cl^- lose their electrons and are oxidized to Cl atoms which combine with each other to form Cl_2 gas.

$$Cl^-_{(g)} \longrightarrow Cl_{(g)} + e^-$$

$$Cl_{(g)} + Cl_{(g)} \longrightarrow Cl_{2(g)}$$

Electron flow through the external circuit from anode to cathode. The electric current is conducted through the cell by the ions and through the external circuit by the electrons. Similarly for fused NaCl, the electrolyte is decomposed during electrolysis. Fused Na is deposited at cathode and $Cl_{2(g)}$ at anode.

(b) Electrolysis of Aqueous Solutions of the Salts

The electrolysis of aqueous solutions of salts is somewhat complicated because of the ability of water, to be oxidized as well as reduced. Some metal cations are not reduced during the electrolysis of their aqueous solutions but water molecules are reduced due to their greater reduction potential as compared to metal cations.

Example: Consider the electrolysis of aqueous solution of sodium nitrate. It ionizes in aqueous solution as

$$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$$

A small concentration of hydronium (H_3O^+) and hydroxyl (OH^-) ions is also formed by the dissociation of water.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

At cathode Na^+ ions are not reduced to metallic Na but H_3^+O ions accept electrons from the cathode and H atoms are formed.

$$H_3O^+_{(aq)} + e^- \longrightarrow H_{(g)} + H_2O_{(l)}$$

H atoms combine to form H_2 gas

$$H_{(g)} + H_{(g)} \longrightarrow H_{2(g)}$$

Although the concentration of H_3O^+ ions is only 10^{-7} $moldm^{-3}$ in pure water but when these H_3O^+ ions are reduced at cathode more H_3O^+ ions are formed by further dissociation of water. Thus, it gives a continuous supply of H_3O^+. Na^+ ions remain in solution. H_2 gas is evolved at cathode. Thus, the reduction of the solute cations depends on the relative ease of the two competing reactions.

At anode: At anode both NO_3^- and OH^- are present. Here oxidation of OH^- ions will take place because its oxidation is easier than NO_3^- ions

$$OH^-_{(aq)} \longrightarrow OH_{(aq)} + e^-$$

The OH groups combine to give O_2 gas at anode

$$4OH_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)}$$

Hydroxyl ions discharge on anode giving oxygen gas and water

Cell reaction

Na^+ ions and NO_3^- ions remain in solution and only water is electrolyzed and forms H_2 and O_2 gases. That is the reason that electrolysis of water occurs only in the presence of an electrolyte

$$2H_2O \longrightarrow 2H_2 + O_2$$

But, remember that the expected order of the discharge of ions may also depend upon their concentrations

Electrolysis Processes of Industrial Importance

Q7. Describe the electrolysis of molten sodium chloride, and a concentrated solution of sodium chloride.

(i) Extraction of sodium by the electrolysis of molten (fused) NaCl (Down's cell)

In this case, electrolysis of molten NaCl is carried out between iron cathode and graphite anode. During the electrolysis, Na metal is obtained at cathode and Cl_2 gas is liberated at anode as by product

$$NaCl_{(s)} \xrightarrow{Heat} Na^+_{(l)} + Cl^-_{(l)}$$

At cathode

$$2Na^+_{(l)} + 2e^- \rightarrow 2Na_{(s)} \text{ (reduction)}$$

At anode

$$Cl^-_{(l)} \longrightarrow Cl_{(g)} + e^- \text{ (Oxidation)}$$

$$Cl_{(g)} + Cl_{(g)} \longrightarrow Cl_{2(g)}$$

Cell Reaction: By adding the two reactions at anode and cathode, the overall reaction is

$$2Na^+_{(l)} + 2Cl^-_{(l)} \longrightarrow 2Na^0_{(s)} + Cl^0_{2(g)}$$

(ii) Preparation of caustic soda by the electrolysis of concentrated aqueous solution of NaCl (Nelson's cell)

Caustic soda is prepared on industrial scale by the electrolysis of aqueous solution of NaCl by using titanium anode and mercury or steel cathode in the Nelson's cell and Castner-Kellner cell or Hg-cell.

$$NaCl_{(s)} \xrightleftharpoons{H_2O} NaCl_{(aq)}$$

$$NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

At anode

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^- \text{ (Oxidation)}$$

At cathode

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)} \text{ (Reduction)}$$

Here Na^+ is not reduced but H_2O molecules are reduced to OH^- and H_2

Cell reaction

$$2Cl^- + 2H_2O \longrightarrow Cl_2 + H_2 + 2OH^-$$

Now including the Na^+ ions on both sides. The reaction can be written as:

$$2Na^+_{(aq)} + 2Cl^-_{(aq)} + 2H_2O_{(\ell)} \longrightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + Cl_{2(g)} + H_{2(g)}$$

Here Cl_2 and H_2 gases are obtained as by products.

(iii) Extraction of Calcium and Magnesium

Calcium and magnesium metals are extracted by the electrolysis of the fused chloride ($CaCl_2$ and $MgCl_2$). Ca^{+2} and Mg^{+2} ions are reduced to Ca and Mg at cathode while Cl_2 gas is liberated at anode.

$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$$

At anode $\quad 2Cl^- \longrightarrow Cl_2 + 2e^-$

At cathode $\quad Mg^{+2} + 2e^- \longrightarrow Mg$

(iv) Extraction of Aluminium

Aluminium is extracted by the electrolysis of fused bauxite ($Al_2O_3.2H_2O$) in the presence of fused cryolite (Na_3AlF_6). This process is called Hall-Beroult process.

The melting point of aluminium oxide is 2045°C but this is decreased using molten cryolite. This reduces the energy requirements.

(v) Preparation of Anodized Aluminium:

Anodized aluminium is prepared by making it an anode in an electrolytic cell containing sulphuric acid or chromic acid which coats a thin layer of oxide on it.

The aluminium oxide layer resists attack for corrosive agents. The freshly anodized aluminium is hydrated and can absorb dyes.

(vi) Purification of Copper

Purification of copper can be carried out in an electrolytic cell using impure copper as anode and a thin sheet of pure copper as cathode. Copper sulphate solution is used as an electrolyte. The atoms of Cu from impure Cu anode are converted to Cu^{2+} ions and migrate to cathode which is made up of pure Cu. In this way Cu anode is purified. Impurities are left at anode.d

(vii) Electroplating

Using various types of electrolytic cells, copper, silver, nickel or chromium plating is done in order to resist rusting. It is called electroplating. In this case metal to be deposited is made as anode and the article to be electroplated is made as cathode. The electrolyte is a soluble salt of the metal to be deposited.

Q16. (g) Impure Cu can be purified by an electrolytic process:

Ans. To purify impure copper, the impure sample is taken as anode while a thin sheet of pure Cu as cathode. Electrolyte is $CuSO_4$ solution and current is passed to perform electrolysis.

Impure Cu anode undergoes oxidation process producing Cu^{+2} ions

$$Cu_{(s)} \rightarrow Cu^{+2}_{(aq)} + 2e^- \quad \text{(oxidation)}$$

These ions move towards cathode where they take up electron and get reduced in the form of Cu-metal.

$$Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \quad \text{(reduction)}$$

In this way impure copper is purified and collected at cathode leaving behind impurities at anode.

Q13. Describe a galvanic cell explaining the functions of electrodes and the salt bridge.

VOLTAIC OR GALVANIC CELL

"A voltaic or a galvanic cell consists of two half-cells that are electrically connected.

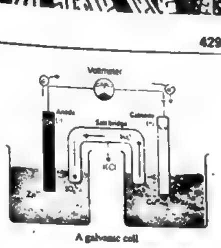
Each half cell is a portion of the total cell in which a half reaction takes place."

The left half-cell consists of a strip of zinc metal dipped in 1 M solution of zinc sulphate giving the following equilibrium.

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$$

The right half-cell is a copper metal strip that dips into 1 M copper sulphate solution and the equilibrium here is represented as follows:

$$Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2e^-$$



A galvanic cell

These half cells are connected electrically by a salt bridge. If the solutions were to mix, direct chemical reactions would take place, destroying the half cells.

The salt bridge contains an aqueous solution of potassium chloride in a gel. Zinc tends to lose electrons more rapidly than copper. Zn electrode takes on a negative charge relative to the copper electrode. If the external circuit is closed by connecting the two electrodes, electrons flow from the zinc through the external circuit to copper electrode. The following half-cell reactions occur at two electrodes and cell potential at standard conditions is 1.1 volts. It is denoted by E°.

At anode

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^- \quad \text{(oxidation)}$$

At cathode

$$Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \quad \text{(reduction)}$$

Remember these charge carriers.
ELECTRONS through the wire;
IONS through the salt bridge

Overall reaction

The overall voltaic cell reaction is the sum of these two half cell reactions.

$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)} \qquad E^\circ = 1.1\ V$$

Representation

The voltaic cell can be represented as follows:

$$Zn_{(s)} / Zn^{+2}_{(aq)} 1M \,||\, Cu^{+2}_{(aq)} 1M / Cu_{(s)} \qquad E^\circ = 1.1\ V$$

- Reduction occurs at copper electrode and oxidation occurs at the zinc electrode.
- Sign || shows the presence of salt bridge.

Explanation

Let us, examine the purpose of the salt bridge. Since, Zinc ions are produced as electrons leave the anode, we have a process which tends to produce a net positive charge in the left beaker. Actually, the concentration of Zn^{+2} ions increase in the left compartment. Similarly, the arrival of the electrons at the copper electrode and their reaction with copper ions tend to produce a net negative charge in the right beaker.

Function of salt bridge

The purpose of the salt bridge is to prevent any net charge accumulation in either beaker by allowing negative ions to leave the right beaker, diffuse through the bridge and enter the left beaker. If this diffusional exchange of ions does not occur, the net charge accumulating in the beakers would immediately stop the flow of electrons through the external circuit and oxidation reduction reaction would stop.

Many other oxidation-reduction reactions can be carried out successfully in galvanic cells using different electrodes. It is natural to think of these cell processes as separated into two half-reactions which occur at the two electrodes.

In a voltaic cell the electric current in the external circuit can be used to light a bulb, drive a motor and so on.

Voltaic cell is reversible cell

On the other hand, if the external circuit is replaced by a source of electricity that opposes the voltaic cell, the external source pushes the electrons in the opposite direction and supplies energy or work to the cell so that the reverse non-spontaneous reaction occurs. Such a cell is called reversible cell. Now, the electrode reactions can be reversed.

Reversed reactions

For a zinc copper cell, the half cell reactions are reversed to give

$$Zn^{+2}_{(aq)} + 2e^- \longrightarrow Zn_{(s)} \quad \text{(reduction)}$$

$$Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2e^- \quad \text{(oxidation)}$$

Overall reaction

The overall reaction being reversed, becomes

$$Zn^{+2}_{(aq)} + Cu_{(s)} \longrightarrow Zn_{(s)} + Cu^{+2}_{(aq)}$$

Oxidation occurs at the copper electrode and reduction takes place at the zinc electrode and the cell operates as an electrolytic cell in which energy from an external source drives a non-spontaneous reaction.

- When a cell operates as a voltaic, the electrode at which reduction occurs is called **cathode**.
- The electrode at which oxidation takes place is called **anode**.

Hence in voltaic cell, Zn acts as a anode and Cu acts as a cathode.

Q16. (e) A salt bridge maintains the electrical neutrality.

Ans. While constructing a typical galvanic cell, two metallic electrodes are dipped in solutions of their ions in two half cells. These half cells are externally connected by an electric circuit and internally by a salt bridge.

A salt bridge is a u-shaped glass tube filled with an aqueous solution of strong electrolyte supported on a gel.

There are three main functions of salt bridge.

(i) It **avoids** the intermixing of liquids of two half cells. If the solutions of two half cells were to mix directly, spontaneous redox reaction will occur destroying the cell so salt bridge is used.

(ii) It **provides** a conducting path between two half cells to continue the passage of electric current.

(iii) It **maintains** electrical neutrality.

During metallic conduction in external circuit from anode to cathode, a net charge accumulation at cathode (-) and anode (+) would results in a voltage drop to zero.

Salt bridge prevents charge accumulation by allowing –ive ions to leave the cathodic half cell, diffuse through it and enters the anodic half cell.

ELECTRODE POTENTIAL

When a metal strip is placed in a solution of its own ions, there are two tendencies.

(i) The metal atoms may dissolve as positive ions. In this way, the electrons are deposited on the metal electrode.

(ii) Metal ions present in the solution may take up electrons from the metal and are deposited as neutral atoms. It imparts a positive charge to the metal.

Thus in both cases, a potential difference is setup between metal and the solution which is called single electrode potential

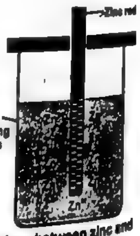
STANDARD ELECTRODE POTENTIAL

"The potential set up when an electrode is in contact with one molar solution of its own ions at 298 K is known as standard electrode potential or standard reduction potential of the element."

It is represented as E°.

Explanation

The electrode potential, setup when a metal piece is dipped in a solution containing the ions of the same metal, can be explained in terms of equilibrium between the atoms of the metal and its ions in the solution. It is believed that when a metal is placed in a solution, some of the atoms of the metal give electrons to the piece of metal and pass into solution as positively charged ions. At the same time the positively charged metal ions present in the solution gain electrons from the piece of metal and are deposited as neutral atom. Depending upon the two tendencies, the metal will become positively or negatively charged as compared to the solution. When equilibrium is attained, the two opposing processes continue at the same rate and there is no further change in the potential difference.



Equilibrium between zinc and its ions in solution

For example, a rod of Zn will have an accumulation of negative charge owing to the net ionization of some of its atoms. This layer of negative charge will attract Zn^{+2} ions around the rod. In this way, an electrical double layer is formed around the Zn rod as shown in figure. The equilibrium state is represented as

$$Zn_{(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2e^-$$

Measurement of electrode potential

The electrode potential of a single electrode can be measured by coupling with a standard half cell whose electrode potential (reduction potential) has been given a convenient value. The electrode chosen as standard for the determination of cell potential of any electrode is a hydrogen electrode

Q8. What is the difference between single electrode potential and standard electrode potential?

Ans.

Single Electrode Potential	Standard Electrode Potential
(i) The potential set up, when an electrode is in contact with the solution of its own ions is called single electrode potential.	(i) The potential setup, when an electrode is in contact with one molar (1M) solution of its own ions at 298K and 1atm. Pressure is called standard electrode potential
(ii) It is measured for any concentration of solution and at any conditions of temperature and pressure.	(ii) It is measured for one molar solution and at standard conditions of temperature and pressure

Q16. (d) Equilibrium is setup between metal atoms of electrodes and ions of metal in the cell.

Ans. This statement is illustrated by studying an example

Consider a Zn-electrode dipped in 1 M solution of $ZnSO_4$, metal atoms from the electrode may oxidize to convert into ions and enter the solution.

$$Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$$

These electrons can be taken by Zn^{+2} ion in solution to become reduced and convert into Zn atom.

$$Zn^{+2}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$$

Initially formation of Zn^{+2} is faster than formation of Zn atom or rate of oxidation is greater than rate of reduction but a time will come when a dynamic equilibrium is established at which rate of both reversible processes become equal

$$Zn_{(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2e^-$$

Q10. Describe the construction and working of standard hydrogen electrode.

Standard Hydrogen Electrode (SHE)

A standard hydrogen electrode consists of a piece of platinum foil, coated with a layer of finally divided platinum black (to give it a large surface area) and is connected with a platinum wire. It is immersed in 1 M HCl solution. Pure H_2 gas at one atmospheric pressure is continuously bubbled into 1 M HCl solution.

The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution. The electrode potential (oxidation or reduction) of this standard hydrogen electrode is arbitrarily taken as zero at all temperatures.

$E^{\circ} = 0.00\ V$

Measurement of electrode potential

The electrode potential of an electrode is measured by dipping the electrode in 1 M solution of its own ions at 25°C. This half cell is now connected with standard hydrogen electrode and a galvanic cell is formed. A voltmeter is inserted in the circuit. The two solutions are separated by a salt bridge or a porous partition. The potential difference is measured by the voltmeter which gives the potential of the electrode under study, as the potential of the standard hydrogen electrode is zero. Ar oxidation or reduction may take place at standard hydrogen electrode depending upon the nature of electrode coupled with it.

Examples

(i) Measurement of Electrode Potential of Zinc

In order to measure the electrode potential of Zn, a galvanic cell is established between Zn electrode dipped in 1 M solution of its own ions and standard hydrogen electrode at 25°C as shown in figure.

Under standard conditions, the voltmeter reads 0.76 volts and the deflection is in such a direction to indicate that Zn has greater tendency to lose electron than Hydrogen. It means that the half reaction

$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$ (oxidation) has a greater tendency to occur than $H_2 \longrightarrow 2H^+ + 2e^-$ by 0.76 volts. The standard electrode potential of Zn is, therefore, 0.76 volts. The electrode reactions are

Electrode potential of zinc

At anode

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$$

At cathode

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

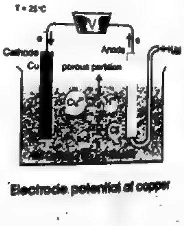
Since, oxidation is taking place at Zn electrode.

So, Oxidation potential of Zn = 0.76 V

Reduction potential of Zn = –0.76 V

(ii) Measurement of electrode potential of copper

In order to measure the electrode potential of Cu, a galvanic cell is formed between Cu electrode dipped in 1 M solution of its own ions and a standard hydrogen electrode as shown in figure. Under standard conditions the voltmeter reads 0.34 volts. The direction of deflection of voltmeter indicates that hydrogen has greater tendency to lose electrons than Cu. In other words, the half reaction $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$ has a greater tendency to occur than the half reaction $Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2e^-$ by 0.34 volts.



Electrode potential of copper

The electrode potential of Cu is, therefore, 0.34 volts. The electrode reactions are

At anode

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$$

At cathode

$$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

Since reduction is taking place at Cu electrode, so

Reduction potential of Cu = 0.34 volts

Oxidation potential of Cu = –0.34 volts

Q16. (b) Standard oxidation potential of Zn is 0.76 volts and reduction potential –0.76 volts.

Ans. Standard oxidation potential of Zn means that Zn has a greater tendency of 0.76 volts than SHE to oxidize or to lose electrons when connected to it.

$$Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^- \quad E^\circ_{oxi} = 0.76 \text{ volts}$$

For the reverse reaction, which is reduction of Zn^{+2} ion by gain of two electrons the E°_{red} is with a reverse sign i.e.,

$$Zn^{+2}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \quad E^\circ_{red} = -0.76 \text{ volts}$$

As both the reactions are opposite to each other, therefore their values of E°_{oxi} and E°_{red} are same but with an opposite sign.

$$Zn_{(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2e^-$$

Q16. (h) SHE acts as anode when connected with Cu-electrode and as cathode when connected to Zn electrode.

Ans. Standard potential of SHE is arbitrarily taken as zero. SHE may undergo an oxidation or reduction depending upon the nature of electrode which is coupled with it.

When SHE is connected to Cu-electrode, it undergoes oxidation and becomes anode while Cu-electrode becomes cathode because reduction potential of copper is greater than SHE.

At cathode: $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (reduction)

At anode: $H_{2(g)} \rightarrow 2H^+ + 2e^-$ (oxidation)

When SHE is connected to Zn-electrode, it acts as cathode and Zn as anode because now SHE has greater reduction potential than Zn-electrode.

At cathode $2H^+ + 2e^- \rightarrow H_2$ (reduction)

At anode $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ (oxidation)

THE ELECTROCHEMICAL SERIES

"When elements are arranged in the order of their standard electrode potential on the hydrogen scale, the resulting list is known as electrochemical series."

Standard Reduction Potentials (E°) of Element at 298 K

Element	Electrode	Standard Reduction Potential (E°)
Li	$Li^+ + e^- \rightarrow Li$	–3.045
K	$K^+ + e^- \rightarrow K$	–2.925
Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	–2.87
Na	$Na^+ + e^- \rightarrow Na$	–2.714
Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	–2.37
Al	$Al^{3+} + 3e^- \rightarrow Al$	–1.66
Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44
Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	–0.403
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25
Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	–0.14
Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	–0.126
H_2	$2H^+ + 2e^- \rightarrow H_2$	0.000
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Cu	$Cu^+ + e^- \rightarrow Cu$	+0.521
I_2	$I_2 + 2e^- \rightarrow 2I^-$	+0.535
Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	+0.771
Ag	$Ag^+ + e^- \rightarrow Ag$	+0.7994
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.885
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.360
Au	$Au^{3+} + 3e^- \rightarrow Au$	+1.50
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

Increasing strength as an oxidizing agent

Increasing strength as a reducing agent (Reference Electrode)

In the electrochemical series shown in table above, the electrode potentials have been given in the reduction mode as recommended by the International Union of Pure and Applied Chemistry (IUPAC).

The table given above shows the standard reduction potential of the elements arranged in the increasing order of the standard reduction potential. The table gives the reduction reactions occurring at the electrode. The electrode will act as cathode.

When the electrode acts as anode i.e., when oxidation is occurring at the electrode, the reaction given in the table is reversed and the sign of the potential will also be reversed *e.g.*, the reduction potential of Zn in the table is –0.76 V. But when Zn acts as anode and oxidation is taking place at Zn electrode, the oxidation potential of Zn will be +0.76 V.

Change in temperature, pressure and concentration will affect the values of reduction potential.

APPLICATIONS OF ELECTROCHEMICAL SERIES

(i) Prediction of the Feasibility of a Chemical Reaction

When we look at the electrochemical series it is easy to predict whether a particular reaction will take place or not.

Example

$Cu^{+2}_{(aq)}$ can oxide solid zinc but $Zn^{+2}_{(aq)}$ cannot oxidize solid copper standard reductions potential values of copper an zinc can explain this:

$$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad E^\circ = +0.34 \text{ volts}$$

$$Zn^{+2}_{(aq)} + 2e^- \longrightarrow Zn_{(s)} \qquad E^\circ = -0.76 \text{ volts}$$

Reverse reaction

Since zinc is being oxidized so the reverse reaction will be considered.

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^- \qquad E^\circ = +0.76 \text{ volts (oxidation)}$$

Overall reaction

The overall reaction will thus be,

$$Cu^{+2}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)} \qquad E^\circ_{cell} = 1.10 \text{ volts}$$

Conclusion

The overall positive value for the reaction potential suggests that the process is energetically feasible. If the sum of E° values of the two half cell reactions is negative then the reaction will not be feasible.

(ii) Calculation of the Voltage or Electromotive (emf) of Cells

In a galvanic cell, the electrode occupying a higher position in the electrochemical series, will act as anode and oxidation takes place on it. Similarly, the electrode occupying the lower position in the series will act as cathode and reduction will take place on it. Let us find out a cell potential or the emf of the cell. The half cell reactions are,

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^- \qquad \text{(oxidation half-cell reaction)}$$

$$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad \text{(reduction half-cell reaction)}$$

Complete cell reaction

$$Cu^{+2}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)}$$

The oxidation potential of Zn is positive. The reduction potential of Cu^{+2} is also positive. The cell voltage or emf of the cell is given by

$$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$$

$$E^\circ_{cell} = 0.76 + 0.34 = 1.10 \text{ volts}$$

Cell voltage

The cell voltage or emf measures the force with which electrons move in the external circuit and therefore measures the tendency of the cell reaction to takes place.

- Galvanic cell thus gives quantitative measures of the relative tendency of the various reactions to occur

(iii) Comparison of Relative Tendency of Metals and non-Metals to get Oxidized or Reduced

The value of the reduction potential of a metal or a non-metal tells us the tendency to lose electrons and act as a reducing agent. It also gives the information about the tendency of a species to gain electrons and act as an oxidizing agent. Greater the value of standard reduction potential of a given species, greater will be its tendency to accept electrons to undergo reduction and hence to act as an oxidizing agent.

For example

Ions like Au^{+3}, Pt^{+2}, Hg^{+2}, Ag^{+}, Cu^{+2} and the non-metal elements like F_2, Cl_2, Br_2 and I_2 which lie below the SHE, have a strong tendency to gain electrons and undergo reduction.

The series tell us that strong oxidizing agents like F_2, Cl_2, Br_2 etc. have a large positive value of standard reduction potentials, while strong reducing agents have large negative values like Li, K, Ca, Na etc, which lie above SHE.

(iv) Relative Chemical Reactivity of Metals

Greater the value of standard reduction potential of a metal, smaller is its tendency to lose electrons to change into a positive ion and hence lower will be its reactivity.

Examples

- Metals like Li, Na, K and Pb are highly reactive (least E°_{red})
- Coinage metals Cu, Ag and Au are the least reactive because they have positive reduction potentials.
- Metals like Pb, Sn, Ni, Co and Cd which are very close to SHE react very slowly with steam to liberate hydrogen gas, (moderately reactive).
- While the metals like Fe, Cr, Zn, Mn, Al and Mg which have more negative reduction potentials react with steam to produce the metallic oxides and hydrogen gas.

(v) Reaction of Metals with Dilute Acids

Greater the value of standard reduction potential of a metal, lesser is its tendency to lose electrons to form metal ions and so weaker is its tendency to displace H_2 from acids.

For example

- Metals like Au, Pt, Ag and Cu which have sufficiently high positive values of reduction potentials, do not liberate hydrogen from acids.
- Metals like Zn, Mg and Ca which are close to the top of the series and have very low reduction potentials liberate hydrogen gas, when they react with acids.

(vi) Displacement of one Metal by another Metal from its Solution

Metal will displace another metal from the aqueous solution of its salt if it lies above the electrochemical series

Examples

- Fe can displace Cu from $CuSO_4$ $(Fe + CuSO_4 \longrightarrow FeSO_4 + Cu)$
- Zn does not displace Mg from solution of $MgSO_4$

Qn. Is the reaction $Fe^{+3} + Ag \longrightarrow Fe^{+2} + Ag^{+1}$ spontaneous? If not, write spontaneous reaction involving these species.

Ans. In this reaction Ag is oxidized and Fe^{+3} is reduced there for the reaction will be

At Anode $\quad Ag^{\circ} \rightarrow Ag^{+1} + 1e^- \quad E^\circ_{oxi} = -0.7994$ volts

At Cathode $\quad Fe^{+3} + 1e^- \rightarrow Fe^{+2} \quad E^\circ_{red} = -0.44$ volts

Spontaneity of a redox reaction can be concluded by calculating E°_{cell}.

$$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$$

$$= (-0.7994) + (-0.44)$$

$$= -1.2394 \text{ volts}$$

If the value of E°_{cell} is negative then the reaction is not feasible and is non-spontaneous.

To make it spontaneous and feasible, the reaction is reversed and cathode-anodes are interchanged i.e.,

$$Ag^{+1} + Fe^{+2} \longrightarrow Fe^{+3} + Ag^\circ$$

At Cathode $Ag^{+1} + 1e^- \rightarrow Ag^\circ$ (reduction) $E^\circ_{red} = +0.7994$ volt

At Anode $Fe^{+2} \rightarrow Fe^{+3} + 1e^-$ (oxidation) $E^\circ_{oxi} = 0.44$ volts

$E^\circ_{cell} = 1.2394$ volts

Therefore the reaction is spontaneous

Q14. (a) Spontaneity of oxidation-reduction reaction.

Ans. Redox reactions are of two types:

(i) Spontaneous redox reactions: Occur on their own without any external assistance when reactants are mixed e.g.,

$$CuSO_4 + Fe \rightarrow Cu + FeSO_4$$

(blue) (green)

(ii) Non-spontaneous redox reaction: Which occur only when an external assistance is applied in the form of electric current e.g.,

$$2NaCl_{(l)} \longrightarrow 2Na_{(s)} + Cl_{2(g)}$$

Spontaneity of a redox reaction can be checked by the calculation of E°_{cell}.

If E°_{cell} is positive then reaction is spontaneous and feasible. This reaction can be used in galvanic cell to generate electric current. For example, during a reaction of $CuSO_4$ and Fe

(Reduction at cathode) $Cu^{+2} + 2e^- \rightarrow Cu$ $E^\circ_{red} = +0.34$ volt

(Oxidation at anode) $Fe \rightarrow Fe^{+2} + 2e^-$ $E^\circ_{oxi} = 0.44$ volt

$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red} = 0.44 + 0.34 = 0.78$ volts

So the following reaction $Cu^{+2} + Fe \rightarrow Fe^{+2} + Cu$ is spontaneous.

And the reaction between $FeSO_4$ and Cu.

$$Fe^{+2} + Cu \rightarrow Cu^{+2} + Fe \qquad E^\circ_{cell} = -0.78 \text{ volts}$$

is a non-spontaneous reaction.

Q15. Will the reaction be spontaneous for the following set of half reactions? What will be the value of E° cell.

(i) $Cr^{+3} + 3e^- \longrightarrow Cr$ $E^\circ_{red} = -0.74V$

(ii) $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{+2} + 2H_2O$ $E^\circ_{red} = 1.28$ V

Ans. Both reactions are reduction type therefore they are not feasible in the same cell. To carry out both reactions in same cell one of the reaction is to be reversed in such a way that $E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$ should be a positive value.

So the following sets of reaction the cell has +ive E°_{cell} value.

At cathode: $[MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{+2} + 2H_2O] \times 3$ (reduction)

At anode: $[Cr^\circ \rightarrow Cr^{+3} + 3e^-] \times 2$ (oxidation)

reduction half reaction $= 3MnO_2 + 12H^+ + 6e^- \rightarrow 3Mn^{+2} + 6H_2O$

oxidation half reaction $= 2Cr \rightarrow 2Cr^{+3} + 6e^-$

Over all reaction: $3MnO_2 + 12H^+ + 2Cr \rightarrow 3Mn^{+2} + 2Cr^{+3} + 6H_2O$

E°_{red} = 1.28 V for reduction half reaction

E°_{oxi} = 0.74 V for oxidation half reaction

So $E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$

$= 1.28 + 0.74 = 2.02$ volts

Q16. (c) Na and K can displace hydrogen from acids but Pt, Pd, Cu cannot why?

Ans. Displacement of hydrogen from acids involve oxidation of metal and reduction of H^+ to H_2 gas from acid.

$M \rightarrow M^+ + 1e^-$ (oxidation)

$2H^+ + 2e^- \rightarrow H_2$ (reduction)

In electrochemical series, those metals which are listed above H_2 have lesser values of reduction potential than H_2 electrode so they possess high values of oxidation potentials.

Na and K possess high values of oxidation potential so they liberate H_2 when react with acids as they are present above H_2 in electrochemical series.

$Na \rightarrow Na^+ + 1e^-$ $E^\circ_{oxi} = 2.714$ volt

$K \rightarrow K^+ + 1e^-$ $E^\circ_{oxi} = 2.925$ volt

On the other hand Pt, Pd, Cu, Au, Ag etc. are listed below H_2 indicating greater reduction potential so they have negative potential to undergo oxidation. e.g.

$Cu \rightarrow Cu^{+2} + 2e^-$ $E^\circ_{oxi} = -0.34$ volt

Therefore these metals are not able to liberate H_2 gas when treated with acids.

LEAD ACCUMULATOR / LEAD ACID BATTERY

- It is commonly used as a car battery.
- It is secondary or a storage cell.
- Passing a direct current through it must charge it.
- The charged cell can then produce electric current when required.

Cathode

The cathode of a fully charged lead accumulator is lead oxide, PbO_2

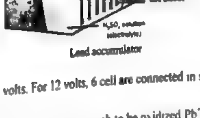
Anode

Its anode is metallic lead (spongy).

Electrolyte

The electrolyte is 30% sulphuric acid solution (density 1.25g cm^{-3})

When the two electrodes are connected through an external circuit, it produces electricity by discharge



Lead accumulator

Voltage

A single cell provides around 2 volts. For 12 volts, 6 cell are connected in series.

Discharging (Galvanic Cell)

At the anode, the lead atoms release two electrons each to be oxidized Pb^{+2} ions, which combine with SO_4^{-2} ions present in the electrolyte and get deposited on the anode as $PbSO_4$

At the cathode

$$PbO_{2(s)} + 4H^{+}_{(aq)} + SO^{-2}_{4(aq)} + 2e^{-} \longrightarrow PbSO_{4(s)} + 2H_2O_{(\ell)} \qquad \text{(reduction)}$$

At the anode

$$Pb_{(s)} + SO^{-2}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^{-} \qquad \text{(oxidation)}$$

The electrons released pass round an external circuit as an electric current to be used for starting the engine of a vehicle, for lighting up of car lights and so on.

At the cathode the electrons from the anode are accepted by PbO_2 and hydrogen ions from the electrolyte then undergo a redox reaction to produce lead ions and water.

The Pb^{+2} ions then combine with SO_4^{-2} ions and they both deposit at the cathode as $PbSO_4$. When both electrodes are completely covered with $PbSO_4$, the cell will cease to discharge any more current until it is recharged.

Overall reaction

The overall reaction is as follows:

$$Pb_{(s)} + PbO_{2(s)} + 4H^{+}_{(aq)} + 2SO^{-2}_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(\ell)}$$

- A typical 12-V car battery have 6-cells connected in series. Each delivers 2V.
- Each cell contains two lead grids packed with the electrode materials.
- The anode is spongy lead and cathode is powdered PbO_2.
- The grid is immersed in an electrolytic solution of ≈ 4.5 M H_2SO_4 (30%).
- Fibre glass sheets between the grids prevent shorting by accidental physical contact.
- When the cell is discharged, it generates electrical energy as a voltaic cell.

Recharging (Electrolytic Cell)

During the process of recharging, the anode and the cathode of the external electrical source are connected to the anode and the cathode of the cell respectively.

The redox reactions at the respective electrodes are then reversed. The reactions are summarized as follows:

At anode

$$PbSO_{4(s)} + 2e^{-} \longrightarrow Pb_{(s)} + SO^{-2}_{4(aq)}$$
(reduction)

At cathode

$$PbSO_{4(s)} + 2H_2O \longrightarrow PbO_{2(s)} + 4H^{+}_{(aq)} + SO^{-2}_{4(aq)} + 2e^{-}$$
(oxidation)

Overall reaction

$$2PbSO_{4(s)} + 2H_2O \longrightarrow Pb_{(s)} + PbO_{2(s)} + 4H^{+}_{(aq)} + 2SO^{-2}_{4(aq)}$$

- During the process of discharging the concentration of the acid falls decreasing its density to 1.15 g cm^{-3}.
- After recharging, the acid is concentrated again bringing its density to its initial value of 1.25 g cm^{-3}.
- At the same time the voltage of the cell, which has dropped during discharging, return to around 12 volts.

Q14. (d) Lead accumulator, its desirable and undesirable features.

Ans. **Desirable features:**

(i) Lead accumulator is a rechargeable battery where cell voltage can be restored by recharging.

(ii) Although the lead accumulator has a very small voltage (12v) but a current of 10A can be produced from it which is comparatively a large current.

Undesirable features:

(i) In theory, charging and recharging can go on indefinitely. However, in actual practice, this is not so H_2SO_4 decomposes and has to be replaced.

(ii) With the passage of time, the plates also change their structure and battery becomes less efficient.

(iii) One of the worst fact is that battery has to spend most of time in discharged state. This causes so much $PbSO_4$ to build up and it is impossible to remove it, so battery has to be changed.

Q16. (a) A porous plate or a salt bridge is not required in lead storage cell.

Ans. There are two reasons for not using a salt bridge in lead storage cell

(i) Both electrodes are dipped in the same solution (30% H_2SO_4) as an electrolyte. If cathode and anode are dipped in two different solutions then salt bridge is used to connect two solutions without chemical mixing to attain electrical neutrality.

(ii) Products of both oxidation and reduction reactions are solids ($PbSO_4$) so there is no chance of their intermixing therefore there is no need of any salt bridge or porous plate in lead storage cell

Q16. (f) Lead accumulator is a chargeable battery

Ans. A **rechargeable galvanic cell** is that cell which after discharging can be recharged by converting into an electrolytic cell.

Lead storage battery is a **rechargeable or secondary galvanic cell.**

During discharging both electrodes of battery are covered with a solid $PbSO_4$, product of reduction at cathode (PbO_2) and oxidation (Pb) at anode in the presence of 30% H_2SO_4 as electrolyte.

Reactions of discharging:

At anode: $Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e^{-}$ (oxidation)

At cathode: $PbO_2 + 4H^{+} + 2e^{-} + SO_4^{-2} \rightarrow PbSO_4 + 2H_2O$ (reduction)

Recharging:

When anode and cathode of external electrical source is connected with anode and cathode of lead storage battery respectively then a reverse non-spontaneous process occur at both electrode and cell voltage is restored.

Reactions during recharging:

Anode will become cathode so the reaction is

$$PbSO_4 + 2e^{-} \rightarrow Pb + SO_4^{-2} \qquad \text{(reduction)}$$

Cathode will become anode so the reaction is

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^{+} + SO_4^{-2} + 2e^{-} \qquad \text{(Oxidation)}$$

So we can say that lead storage battery is rechargeable.

Q14. (c) Write comprehensive notes on alkaline, silver oxide and nickel-cadmium batteries, fuel cell.

ALKALINE BATTERY (NON-RECHARGEABLE)

In the dry alkaline cell Zn rod is used as the anode and manganese dioxide (MnO_2) is used as the cathode. A base KOH is used as an electrolyte due to which it is known as alkaline battery. The battery is enclosed in a steel container. Porous Zn is used to provide it a large effective area. It allows to produce more electrical current as compared to common dry cells. It is a long life cell. The reactions which occur are

At anode

$$Zn_{(s)} + 2OH^{-}_{(aq)} \longrightarrow Zn(OH)_{2(s)} + 2e^{-} \qquad \text{(oxidation)}$$

At cathode

$$2MnO_{2(s)} + H_2O + 2e^{-} \longrightarrow Mn_2O_{3(s)} + 2OH^{-}_{(aq)} \text{(reduction)}$$

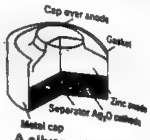
Cell reaction

$$Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(\ell)} \longrightarrow Zn(OH)_{2(s)} + Mn_2O_{3(s)}$$

The voltage of this cell is 1.5 volts.

SILVER OXIDE BATTERY

These are tiny and expensive batteries, commonly used in electronic watches, auto exposure cameras and electronic calculators. In this battery silver oxide (Ag_2O) is used as cathode and Zn metal is used as anode. A basic electrolyte like NaOH or KOH is used. Following reactions occur:



A silver oxide battery

At anode

$$Zn_{(s)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(s)} + 2e^- \quad \text{(oxidation)}$$

At cathode

$$Ag_2O_{(s)} + H_2O_{(\ell)} + 2e^- \longrightarrow 2Ag_{(s)} + 2OH^-_{(aq)} \quad \text{(reduction)}$$

Cell reaction

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(\ell)} \longrightarrow 2Ag_{(s)} + Zn(OH)_{2(s)}$$

The voltage of cell is 1.5 V.

NICKEL CADMIUM CELL (NICAD) (RECHARGEABLE)

A strong cell which is widely used in recent years is the NICAD or nickel cadmium battery. The anode is made of Cd and cathode is composed of NiO_2. In this cell an alkaline electrolyte is used. Following reactions occur:

At anode

$$Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2e^- \quad \text{(oxidation)}$$

At cathode

$$NiO_{2(s)} + 2H_2O_{(\ell)} + 2e^- \longrightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)} \quad \text{(reduction)}$$

Cell reaction

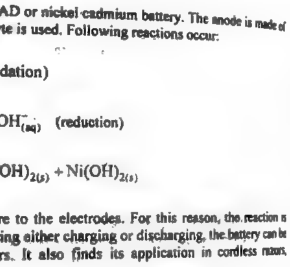
$$Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(\ell)} \longrightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}$$

The voltage of this cell is 1.4 V.

Just like lead storage cell, the solid reaction products adhere to the electrodes. For this reason, the reaction is easily reversed during recharging. Because no gases are produced during either charging or discharging, the battery can be sealed. It is used in battery operated tools and portable computers. It also finds its application in cordless razors, photoflash units.

FUEL CELLS (RECHARGEABLE)

Fuel cells are similar to Galvanic cells by which chemical energy may be converted into electrical energy. In fuel cells gaseous fuels such as hydrogen and oxygen are allowed to undergo a reaction to produce electrical energy. The electrodes are hollow tubes which are made of porous compressed carbon impregnated with platinum which acts as a catalyst. The electrolyte is KOH. At the electrodes, hydrogen is oxidized to water and oxygen is reduced to hydroxide ions.



Hydrogen - Oxygen Fuel cell

$$\left[H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(\ell)} + 2e^-\right] \times 2 \quad \text{(anode)}$$

$$O_{2(g)} + 2H_2O_{(\ell)} + 4e^- \longrightarrow 4OH^-_{(aq)} \quad \text{(cathode)}$$

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(\ell)} \quad \text{(overall reaction)}$$

Such a cell runs continuously as long as reactants are supplied.

Importance of fuel cell

These fuel cells are used in space vehicles. This fuel cell is operated at high temperature so that wa. formed as a product of cell reaction evaporates and may be condensed and used as drinking water by the space astronaut. A number of these cells are usually connected with each other for the generation of several kilowatt of power.

The fuel cells produce electricity and pure water during space flights. Fuel cells are light, portable and sources of electricity. Many fuel cells do not produce pollutants. Some other cell reactions in fuel cell are:

$$2NH_3 + 3/2O_2 \longrightarrow N_2 + 3H_2O_{(\ell)}$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O_{(\ell)}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O_{(\ell)}$$

Fuel cells are very efficient. They convert about 75% of fuels bond energy into electricity

DIFFERENT BATTERIES

Particulars	Alkaline battery	Ag_2O battery	Ni-Cd cell	Fuel cell
Definition	Dry, non-rechargeable	Expensive, used in auto cameras	Strong cell, rechargeable	Change chemical energy into electrical energy, rechargeable
Anode	Zn rod	Zn metal	Cadmium	Porous carbon impregnated with Pt
Cathode	MnO_2	Ag_2O mixed with NaOH	NiO_2	Porous carbon impregnated with Pt
Capacity	1.5V	1.5V	1.4V	75% bond energy into electricity
Uses	Toys, watches, tape recorder etc.	Battery, electronic watches, auto exposure camera etc	Mobile phones	Used in rocket as a fuel cell
Others	Electrolyte is basic	Electrolyte is basic	Electrolyte is basic	KOH is electrolyte. It operates at high temperature.
Overall Reactions	$Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(l)} \rightarrow Zn(OH)_{2(s)} + Mn_2O_{3(s)}$	$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn(OH)_2 + 2Ag_{(s)}$	$Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}$	$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

KEY POINTS

1. Electrochemistry is the branch of science which deals with the conversion of electrical energy to chemical energy and vice versa.
2. Electrolytic conduction is carried out by the ions produced when an ionic compound is in fused state or dissolved in water. Electrolysis is the process in which a chemical reaction takes place at the expense of electrical energy. Electrolysis is used for the extraction of elements and for the commercial preparation of several compounds. It is also used for electroplating.
3. A Galvanic or a voltaic cell produces electrical energy at the expense of chemical energy. Electrode potential is developed when a metal is dipped into a solution of its own ions.
4. The potential of standard hydrogen electrode is arbitrarily fixed as 0.00 volts. Electrode potential of an element is measured when it is coupled with standard hydrogen electrode. When elements are arranged in order of their standard electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series. Electrochemical series is used to predict the feasibility of a redox chemical reaction.

5. Modern batteries and fuel cell include lead accumulator, alkaline battery, silver oxide battery, nickel cadmium cell and hydrogen oxygen fuel cell.

6. The oxidation number is the apparent charged which an atom has in a molecule. Redox chemical equations can be balanced using oxidation number method and ion electron method.

SOLVED OBJECTIVE EXERCISE

Q1. Multiple choice questions:

(i) The cathodic reaction in the electrolysis of dil.H_2SO_4 with Pt electrode is:
(a) Reduction (b) Oxidation (c) Both reduction, oxidation (d) Neither reduction nor oxidation

(ii) **Which of the following statement is not correct about galvanic cell?**
(a) Anode is –ively charged (b) Reduction at anode
(c) Cathode is +ively charged (d) Reduction at cathode

(iii) Stronger the oxidizing agent, greater is the:
(a) Oxidation potential (b) Reduction potential (c) Redox potential (d) e.m.f of cell

(iv) If the salt bridge is not used between two half cells, then the voltage:
(a) Decreases rapidly (b) Decreases slowly (c) Does not change (d) Drops to zero

(v) If a strip of Cu metal is placed in a solution of $FeSO_4$:
(a) Cu will be deposited (b) Fe is precipitated out (c) Cu and Fe both dissolve (d) No reaction takes place

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(a) Reduction	Usually during electrolysis the reaction takes place at cathode is reduction reaction. Pt is an inert electrode.
(ii)	(b) Reduction at anode	In galvanic / voltaic cell, at anode oxidation takes place.
(iii)	(b) Reduction potential	Greater the value of standard reduction potential of a given species, greater will be its tendency to accept electrons to undergo reduction and hence to act as an oxidizing agent.
(iv)	(d) Drops to zero	A salt bridge maintains the electrical neutrality. It provides a conducting path between two half cells to continue the passage of electric current. During metallic conduction in external circuit from anode to cathode, a net charge accumulation at cathode (-) and anode (+) would results in a voltage drop to zero.
(v)	(d) No reaction takes place	Metal will displace another metal from the aqueous solution of its salt if it lies above the electrochemical series. Fe can displace Cu from $CuSO_4$ because Fe lies above the Cu in electrochemical series but Cu cannot displace Fe from $FeSO_4$. As a result if a strip of Cu metal is placed in a solution of $FeSO_4$, no reaction takes place.

Q2. Fill in the blanks:

(i) The oxidation number of O-atom is ________ in OF_2 and ________ in H_2O_2.
(ii) Conductivity of metallic conductors is due to flow of ________ while that of electrolyte is due to flow of ________.
(iii) Reaction taking place at the ________ is termed as oxidation and at the ________ is reduction.
(iv) ________ is setup when a metal is dipped in its own ions.
(v) Cu metal ________ at the Cu-cathode when electrolyte is performed for $CuSO_4$ solution with Cu-cathode.
(vi) The reduction potential of Zn is ________ volts and its oxidation potential is ________ volts.
(vii) In the fuel cell ________ react together in the presence of ________.

ANSWERS

(i) +2, -1	
(iii) anode, cathode	(ii) electron, ion
(v) deposits at	(iv) potential difference
(vii) H_2 and O_2, KOH	(vi) –0.76, +0.76

Q3. Tick true and false:

(i) In electrolytic conduction, electrons flow through the electrolyte.
(ii) In the process of electrolysis, the electron in the external circuit flow from cathode to anode
(iii) Sugar is a non-electrolyte in solid form and when dissolved in water will allow the passage of electric current.
(iv) A metal will only allow the passage of electric current when it is in cold state.
(v) The electrolytic products of aqueous copper (II) chloride solution are copper and chlorine.
(vi) Zinc can displace iron from its solution.
(vii) SHE acts as cathode when connected with Cu-electrode.
(viii) A voltaic cell produces electrical energy at the expense of due to chemical energy.
(ix) Lead storage battery is not a reversible battery
(x) Cr changes its oxidation number when $K_2Cr_2O_7$ is reacted with HCl

ANSWERS

(i) False	(ii) False	(iii) False	(iv) True	(v) True
(vi) True	(vii) False	(viii) True	(ix) False	(x) True

SHORT ANSWERS TO EXERCISE

Q10. Out line construction and working of SHE.

Ans. SHE stands for "Standard Hydrogen Electrode."

Construction of SHE:

Electrode: Piece of platinum foil which is electrolytically coated with finely divided platinum, black to increase its surface area, platinum acts as electrical conductor. H_2 gas at one atmospheric pressure is bubbled at the electrode in electrolyte.

Electrolyte is 1M HCl solution

An equilibrium is present between gas and its ions in this half cell as

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

Standard potential of SHE: Potential of this electrode is arbitrarily taken as zero.

Working of SHE: SHE is used to measure the electrode potential of any element. It is done by coupling the SHE with concerned electrode through a salt bridge forming a galvanic cell.

Potential difference is measured by a voltmeter. An oxidation or reduction may take place at SHE depending upon nature of electrode coupled.

Example:

(i) When SHE is connected with Zn-electrode, SHE becomes cathode and Zn-anode with an oxidation potential of 0.76 volts for Zn.

(ii) On the other hand if SHE is connected with Cu electrode, SHE becomes anode and Cu-cathode shows a reduction potential of 0.34 volts.

Additional Questions

Q. Differentiate between oxidizing agent and reducing agent.

Ans.

Oxidation Agent	Reduction Agent
(i) A specie which oxidize a substance in a redox reaction is called an oxidizing agent or oxidant.	(i) A specie which reduces a substance in a rodax reaction is called as a reducing agent or reductant
(ii) In the process, the oxidizing agent is reduced itself	(ii) In the process, the reducing agent is oxidized itself.
(iii) An oxidizing agent gain electrons and its oxidation number decreases in the reaction. e.g., $KMnO_4 / H_2SO_4$, $K_2Cr_2O_7 / H_2SO_4$ HNO_3, Cl_2, Br_2 etc.	(iii) The reducing agent lose electrons and its oxidation number is increased. e.g., $FeSO_4, HI, SO_2, Na, K$ etc.

Q. Why alkali metals react vigorously with water while coinage metals does not react.

Ans. Smaller the value of reduction potential, greater is its tendency to lose electron and hence greater is its reactivity.

Na, K, Rb have small values of standard reduction potentials, so these are highly reactive metals. Therefore these metals react vigorously with water and liberate H_2 gas.

$$2Na_{(s)} + 2H_2O_{(\ell)} \rightarrow 2NaOH_{(aq)} + H_{2(g)} \uparrow$$

Coinage metals (Cu, Ag, Au) have high positive values of reduction potential. So these metals have very little tendency to lose electrons and are considered as least reactive metals. These metals cannot reduce water to liberate hydrogen gas.

$$Cu_{(s)} + H_2O_{(\ell)} \rightarrow \text{No reaction}$$

Q. Differentiate between primary and secondary cells.

Ans.

Primary Cell	Secondary Cell
(i) Those galvanic cells which cannot be recharged are called as primary cells.	(i) Those galvanic cells which can be recharged are called as secondary cells.
(ii) the electrode reactions are irreversible.	(ii) The electrodes reactions can be reversed by supplying electrical energy.
(iii) Examples: Alkaline battery. Silver oxide battery.	(iii) Examples: Lead accumulator. Daniel Cell.

Q. What is emf and how we calculate the emf of a galvanic cell.

Ans. **Electromotive force or emf:**

The force with which electrons moves from anode towards the cathode through an external circuit in a galvanic cell is called the electromotive force (emf).

It measures the tendency of the cell reaction to takes place.

Calculation of emf of a Cell:

- Let us find the emf or cell potential of Daniel cell. The half-cell reactions are.

$$Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^- \quad \text{(Oxidation half)}$$

$$Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \quad \text{(Reduction half)}$$

The overall cell reaction is

$$Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Cu_{(s)} + Zn^{+2}_{(aq)}$$

The cell voltage or emf of the cell is given by

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$
$$= 0.76V + 0.34V$$
$$= 1.10V$$

Important Previous Board Questions

Q. How anodized aluminium is prepared?

Q. What is the difference between a cell and a battery?

Q. What is emf of a Cell?

Q. Alkali metals like (Li, Na, ...) are easily oxidized while coinage metals (Cu, Ag, Au) are not easily oxidized. Why?

Q. Give conditions of electric conduction through electrolytes.

For Answers study Scholar's CHEMISTRY (Objective) XI

REACTION KINETICS

REACTION KINETICS

"The branch of chemistry which deals with rates of chemical reactions, factors that affect the rates of chemical reactions and the mechanisms of reactions is called reaction kinetics."

Rate of reaction

"The change in the concentration of a reactant or a product divided by the time taken for the change is called rate of reaction."

$$\text{Rate of reaction} = \frac{\text{change in concentration of the substance}}{\text{time taken for the change}}$$

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t}$$

Units

(i) $$\text{Rate of reaction} = \frac{\text{mol.dm}^{-3}}{\text{s}}$$

$$\text{Rate} = \text{mol.dm}^{-3}.\text{s}^{-1}$$

(ii) In case of gases, concentration is taken in partial pressure. So,

$$\text{Rate of reaction} = \frac{\text{atm}}{\text{s}}$$

$$\text{Rate} = \text{atm.s}^{-1}$$

Examples of reactions with different rates

(i) Many reactions, in aqueous solutions, are so rapid that they seem to occur instantaneously. For example, a white precipitate of silver chloride is formed immediately on addition of silver nitrate solution to sodium chloride solution.

(ii) Some reactions proceed at a moderate rate e.g. hydrolysis of an ester.

(iii) Still other reactions take a much longer time, for example, the rusting of iron, the chemical weathering of stone work of buildings by acidic gases in the atmosphere and the fermentation of sugars.

Importance of rate of reaction

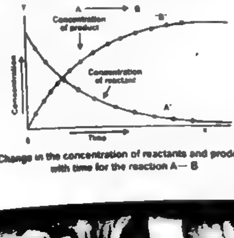
The rate of reactions and their control are often important in industry. They might be the deciding factors that determine whether a certain chemical reaction may be used economically or not.

Graphical explanation

During a chemical reaction, reactants are converted into products. So, the concentration of the products increases with the corresponding decrease in the concentration of the reactants as they are being consumed.

This graph is plotted for a reaction in which reactant A is changing irreversibly to the product B

$$A \longrightarrow B$$



Change in the concentration of reactants and products with time for the reaction A → B

The slope of the graph for the reactant or the product is the steepest at the beginning. This shows a rapid decrease in the concentration of the reactant and consequently a rapid increase in the concentrations of the product. As the reaction proceeds, the slope becomes less steep indicating that reaction is slowing down with time.

From the graph it is obvious that

(i) The change in the concentration of the reactant A or the product B is much more at the start of reaction and then it decreases gradually.

(ii) The rate of reaction decreases with time.

(iii) The rate of a reaction never remains uniform during different time intervals i.e. it is changing every moment.

(iv) It decreases continuously till the reaction ceases.

$$\text{Rate} = -\frac{\Delta A}{\Delta t} = \frac{\text{change in concentration of reactants}}{\text{time taken for the change}}$$

$$\text{Rate} = +\frac{\Delta B}{\Delta t} = \frac{\text{change in concentration of products}}{\text{time taken for the change}}$$

Differences between instantaneous rate and average rate

Instantaneous rate	Average rate
The rate at any one instant during the interval is called the instantaneous rate.	The rate of reaction between two specific time intervals is called average rate.
Instantaneous rate $= \frac{dx}{dt}$	Average rate $= \frac{\Delta x}{\Delta t}$
At first, the instantaneous rate is higher than the average rate.	At the end, average rate is higher than instantaneous rate.

As the time interval becomes smaller, the average rate becomes closer to the instantaneous rate. The average rate will be equal to the instantaneous rate when the time interval approaches zero. Thus the rate of reaction is instantaneous change in the concentration of a reactant or a product at a given moment of time.

Q8. (i) *Rate of reaction is an ever changing parameter.*

Ans. ***According to law of mass action:***

"Rate of a chemical reaction is directly proportional to the product of active masses of reactants."

Rate of reaction is very fast at the beginning due to greater concentration of reactants. But gradually rate goes on decreasing as the concentration of reactants decreases every moment. Therefore the rate of a reaction changes at every instant or it is an ever changing parameter.

Specific Rate Constant or Velocity Constant (k)

According to law of mass action:

"The rate of a chemical reaction is directly proportional to the active mass of the reactant or to the product of active masses if more than one reactants are involved in a chemical reaction."

Note

For a dilute solution, the active mass is considered as equal to concentration.

Consider the general reaction,

$$aA + bB \longrightarrow cC + dD$$

According to law of mass action,

rate of reaction $\propto [A]^a[B]^b$ Rate $= k[A]^a[B]^b$

This equation is called rate equation or rate law. The brackets [ ] represent the concentration in $mol.dm^{-3}$. 'k' is called specific rate constant or velocity constant.

Suppose,

$[A] = 1\ mol.dm^{-3}$

$[B] = 1\ mol.dm^{-3}$

then **Rate of reaction $= k \times 1^a \times 1^b$**

So, Rate of reaction = k

Hence,

"The specific rate constant of a reaction is the rate of the reaction when concentration of reactants are in unity."

or

"The proportionality constant which relates concentrations of reactants with rate of reaction."

Characteristics of rate constants

1. The value of k is different for different reactions.
2. It is a measure of intrinsic rate of reaction. This means larger the value of k, faster will be the reaction. Similarly, small value of k reflects slower reaction.
3. At a fixed temperature, the value of k is a constant and characteristic of a reaction
4. For a particular reaction, k is independent of concentration but depends on temperature

Q8. (ii) Reaction rate decreases every moment but the rate constant "k" of a reaction is a constant quantity in given conditions.

Ans. Consider a reaction:

$$A + B \longrightarrow \text{Products}$$

According to law of mass action the rate is given by

Rate $= k[A][B]$

or $k = \frac{\text{Rate}}{[A][B]} = \frac{\text{Rate}}{\text{conc. of reactants}}$

As the reaction progresses, rate of reaction decreases due to decrease in concentration of reactants but rate constant remains constant as it is the ratio of rate of reaction to concentration of reactants.

Q7. (i) Differentiate between rate of reaction and rate constant.

Ans.

Rate of reaction	Rate constant
(i) It is the speed at which the reactants are converted into the products.	It is a constant of proportionality in the rate law expression.
(ii) Rate $= \frac{\Delta x}{\Delta t}$	Rate = k[Reactants] $k = \frac{\text{Rate}}{[\text{Reactants}]}$
(iii) It depends upon the concentration of reactant species at that moment.	It refers to the rate of reaction at specific point when concentration of every reacting species is unity
(iv) It decreases with the progress of reaction generally.	It is a constant and does not depend on the progress of the reaction.

ORDER OF REACTION

"The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction."

or

"The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction."

Mathematical expression

$$\underset{\text{reactants}}{aA + bB} \longrightarrow \underset{\text{products}}{cC + dD}$$

Rate equation for this reaction is,

Rate of reaction $= k[A]^a[B]^b$

Order of reaction $= a + b$

Note

The exponent "a" or "b" in the rate equation gives the order of reaction with respect to the individual reactant. Thus, the reaction is of order "a" with respect to "A" and of "b" with respect to "B".

Important points

- The order of reaction is an experimentally determined quantity and cannot be calculated simply by looking at the reaction equation.
- Order of reaction provides us valuable information about the mechanism of a reaction.
- The order of a reaction may be positive, negative, zero or in fraction.

The general form of a rate equation is

$$rate = k[A]^m[B]^n$$

where

- k is the rate constant for the reaction.
- m and n are the orders of reaction with respect to the reactants A and B.
- the overall order = m + n

Zero Order Reaction

"The reaction which is entirely independent of the concentration of reactant molecules is called zero order reaction."

Mathematical expression

$$A \longrightarrow Product$$

$$Rate = k[A]^0 \qquad (\text{"zero" sign indicates no change in concentration})$$

So, $Rate = k$

Examples

(i) All photochemical reactions are usually zero order reactions.

(ii) $H_2 + Cl_2 \xrightarrow{(darkness)} \text{no reaction}$

$H_2 + Cl_2 \xrightarrow{sunlight} 2HCl$

(iii) $2NH_3 \xrightarrow{Pt} N_2 + 3H_2$

Negative-order reactions are rare, for example the conversion of ozone (order 2) to oxygen (order −1).

Units of k

$$k_{(o)} = mol.dm^{-3}.s^{-1}$$

First Order Reaction

"The reaction in which the molar concentration of only one molecule alters as a result of chemical change is called first order reaction."

Mathematical expression

$$A \longrightarrow Product$$

$$Rate = k[A]^1$$

Order of reaction = 1

Example

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

Rate equation for this reaction is

$$Rate = k[N_2O_5]^1$$

Order of reaction = 1

Reaction completes in two steps:

$$N_2O_5 \xrightarrow{Slow} N_2O_4 + [O]$$

$$N_2O_5 + [O] \xrightarrow{Fast} N_2O_4 + O_2$$

Units of k_1

$$Rate = k[A]$$

$$k_1 = \frac{Rate}{[A]} = \frac{mol.dm^{-3}.s^{-1}}{mol.dm^{-3}} = s^{-1}$$

Second Order Reaction

"The reaction in which the molar concentrations of two reactant molecules alter as a result of chemical change is called second order reaction."

Mathematical Expression

$$A + A \longrightarrow Product$$

Rate of reaction $= k[A]^2$

Order of reaction = 2

Examples

(i) $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$

Rate equation $= k[H_2]^1[I_2]^1$

Order of reaction = 1 + 1 = 2

(ii) $NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$

Rate of equation $= k[NO]^1[O_3]^1$

Order of reaction = 1 + 1 = 2

Units of k_2

$$k_2 = \frac{Rate}{[A]^2} = \frac{mol.dm^{-3}.s^{-1}}{mol.dm^{-3}.mol.dm^{-3}}$$

$$k_2 = mol^{-1}.dm^{+3}.s^{-1}$$

Q8. (v) The unit of rate constant of a 2nd order reaction is $dm^3\ mol^{-1}\ s^{-1}$ but the unit of rate of reaction is $mol\ dm^{-3}\ s^{-1}$.

Ans. Rate of a reaction is defined as change in concentration of a substance divided by time taken for that change i.e.,

$$Rate = \frac{\Delta x}{\Delta t}$$

Unit of concentration is $mol\ dm^{-3}$ and unit of time is second(s). So unit of rate of reaction is obvious i.e.,

$$Rate = \frac{\Delta x}{\Delta t} = \frac{mol\ dm^{-3}}{s}$$

$$= mol\ dm^{-3}\ s^{-1}$$

On the other hand, consider a second order reaction.

$$A + B \longrightarrow Product$$

The rate of this reaction is given by $Rate = k[A]^1[B]^1$

$$k = \frac{Rate}{[A][B]}$$

To calculate the unit of K, rate unit $mol\ dm^{-3}\ s^{-1}$ is divide by units of concentration for A, B reactants.

$$k = \frac{mol\ dm^{-3}s^{-1}}{(mol\ dm^{-3})(mol\ dm^{-3})} = mol^{-1}dm^3s^{-1}$$

$$= dm^3\ mol^{-1}\ s^{-1}$$

So, it is proved that unit of

$$k = dm^3\ mol^{-1}\ s^{-1} \text{ (for 2nd order)}$$

Third Order Reaction

"The reaction in which the molar concentrations of three reactant molecules alter as a result of the chemical change is called third order reaction."

Mathematical Expression

$$3A \longrightarrow \text{Product}$$

$$\text{Rate of reaction} = k[A]^3$$

$$\text{Order of reaction} = 3$$

Example

(i)

$$2FeCl_3 + 6KI \longrightarrow 2FeI_2 + 6KCl + I_2$$

$$\text{Rate of reaction for this reaction} = k[FeCl_3]^1[KI]^2$$

$$\text{Order of reaction} = 1 + 2 = 3$$

So, above reaction is 3rd order reaction.

Mechanism of reaction

$$FeCl_{3(aq)} + 2KI_{(aq)} \xrightarrow{\text{Slow}} FeI_{2(aq)} + 2KCl_{(aq)} + Cl^-_{(aq)}$$

$$2KI_{(aq)} + 2Cl^-_{(aq)} \xrightarrow{\text{Fast}} 2KCl_{(aq)} + I_{2(s)}$$

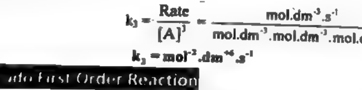
Units of k_3

$$k_3 = \frac{\text{Rate}}{[A]^3} = \frac{mol.dm^{-3}.s^{-1}}{mol.dm^{-3}.mol.dm^{-3}.mol.dm^{-3}}$$

$$k_3 = mol^{-2}.dm^{+6}.s^{-1}$$

Pseudo First Order Reaction

Hydrolysis of tertiary butyl bromide.



The rate equation determined experimentally for this reaction is:

$$\text{Rate} = k[(CH_3)_3CBr]$$

The rate of reaction remains effectively independent of the concentration of water because being a solvent, it is present in very large excess. Such type of reactions have been named as pseudo first order reaction.

Fractional Order Reaction

The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value.

Example

Consider the formation of carbon tetrachloride from chloroform.

$$CHCl_{3(l)} + Cl_{2(g)} \longrightarrow CCl_{4(l)} + HCl_{(g)}$$

$$\text{Rate} = k[CHCl_3]\ [Cl_2]^{1/2}$$

The sum of exponents will be $1 + 1/2 = 1.5$ so,

$$\text{Order of reaction} = 1.5$$

Q8. (vi) The sum of coefficients of a balanced equation is not necessarily important to give order of reaction.

Ans. Order of a chemical reaction is not necessarily the sum of the coefficients of the balanced chemical equation because the order of reaction is determined experimentally and not from the balanced chemical equation.

e.g., $2H_2 + 2NO_2 \longrightarrow 2H_2O_2 + N_2$

For this reaction, the sum of coefficients of balanced equation is $2 + 2 = 4$ but the reaction is 3rd order. It is experimentally verified that rate of reaction is directly related to conc. of H_2 and to the square of concentration of NO_2. So the rate equation of this reaction is

$$\text{Rate} \propto [H_2]^1[NO_2]^2$$

$$\text{Rate} = k[H_2]^1[NO_2]^2$$

Order of reaction is sum of exponents of rate equation. So

$$\text{Order of reaction} = 1 + 2 = 3$$

Q8. (vii) The order of reaction is obtained from the rate expression but the rate expression is obtained from experiment.

Ans. The rate expression can only be obtained experimentally. It represents the actual dependence of rate on concentrations of the reactants. A reactant whose concentration does not effect the rate of reaction is not included in the rate equation. The order of the reaction is number of reactant molecules whose concentrations alter as a result of chemical reaction. So the order is obtained by rate expression and rate is determined experimentally.

Half-Life Period

"The time which is required to convert 50% of the reactants into products is called half-life period ($t_{1/2}$)."

Examples

(i) Decomposition of N_2O_5

The half-life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

$$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$$

$t_{1/2} = 24$ min at 45°C
[1st order reaction]

It means that if we decompose 0.1 $mol.dm^{-3}$ of N_2O_5 at 45°C, then after 24 min 0.05 $mol.dm^{-3}$ of N_2O_5 will be left behind. Similarly, after 48 min 0.025 (25%) $mol.dm^{-3}$ of N_2O_5 will remain unreacted and after 72 min (3 half times) 0.012 (12.5%) $mol.dm^{-3}$ of N_2O_5 will remain unreacted.

The half-life period of 1st order reaction does not depend upon the initial concentration of reactant.

(ii) Disintegration of $^{235}_{92}U$

The disintegration of radioactive $^{235}_{92}U$ has a half-life of 7.1×10^8 or 710 million years. If one kilogram sample disintegrates, then 0.5 kg of it is converted to daughter elements in 710 million years. out of 0.5 kg of $^{235}_{92}U$, 0.25 kg disintegrates in the next 710 million years. so the half life period for the disintegration of a radioactive substance is independent of the amount of that substance.

Half life period and order of reaction

The half life period of any order reaction is inversely proportional to the initial concentration raised to the power one less than order of that reaction

$$[t_{1/2}]_n = \frac{1}{a^{n-1}}$$

where, $t_{1/2}$ = half-life period
n = order of reaction
a = initial concentration of reactant

For first order reaction

$$n = 1$$

$$[t_{1/2}]_1 \propto \frac{1}{a^{1-1}}$$

$$[t_{1/2}]_1 \propto \frac{1}{a^0}$$

Since $[t_{1/2}]_1 = \dfrac{0.693}{k}$

For second order reaction

$$n = 2$$

$$[t_{1/2}]_2 \propto \frac{1}{a^{2-1}}$$

$$[t_{1/2}]_2 \propto \frac{1}{a^1}$$

Since $[t_{1/2}]_2 = \frac{1}{ka}$

Note

In case of second order reaction, the half-life period is inversely proportional to the initial concentration of the reactant.

For third order reaction

$$n = 3$$

$$[t_{1/2}]_3 \propto \frac{1}{a^{3-1}}$$

$$[t_{1/2}]_3 \propto \frac{1}{a^2}$$

Since $[t_{1/2}]_3 = \frac{1.5}{ka^2}$

For a third order reaction, the half life period is inversely proportional to the square of initial concentration of reactants.

Q8. (iii) 50% of hypothetical 1st order reaction completes in one hour. The remaining 50% needs more than one hour to complete.

Ans. The half life of 1st order reaction is independent of the initial concentration of reactants.

$$[t_{1/2}]_1 \propto \frac{1}{a^0}$$

For a hypothetical reaction, the half life is one hour, it means 50% of that reaction is completed in first hour.

In the next one hour $50 \times \frac{50}{100} = 25\%$ of reaction completes

In the still next hour $50 \times \frac{25}{100} = 12.5\%$ of reaction completes and so on. So, in order to get 100% completion of reaction, many hours are required rather than only one hour.

Q8. (iv) The radioactive decay is always a 1st order reaction.

Ans. A radioactive substance has a single species at a moment, whose nucleus undergoes disintegration. As only one reactant is involved, so it follows 1st order mechanism.

e.g., Half life of $^{235}_{92}U$ is 710 million years. It means if one kg uranium is present at start, after 710 million years, 0.5 kg of it will disintegrate and after next 710 million years 0.25 kg of it will disintegrate and so on.

Therefore we can say that half life of a radioactive decay is always a 1st order reaction.

Rate Determining Step

"Rate-determining step is that step of a chemical reaction which controls the rate of reaction."

If a reaction occurs in several steps, one of the steps is the slowest. The rate of this step determines the overall rate of reaction. This slowest step is called the rate determining or rate limiting step. The total number of molecules taking part in the rate determining step appear in the rate equation of the reaction.

Let us consider the following reaction

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

The rate equation of the reaction is found to be

$$Rate = K[NO_2]^2$$

The reaction is second order with respect to $NO_{2(g)}$. Experiment shows that $CO_{(g)}$ is not taking part in the rate determining step. The proposed mechanism for this reaction is as follows:

$$NO_{2(g)} + NO_{2(g)} \xrightarrow{Slow} NO_{3(g)} + NO_{(g)} \quad \text{(Rate determining step)}$$

$$NO_{3(g)} + CO_{(g)} \xrightarrow{Fast} NO_{2(g)} + CO_{2(g)}$$

The first step is the rate determining step and NO_3 which does not appear in the balanced equation, is called the reaction intermediate. The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products.

Q7. (iii) Differentiate between fast step and rate determining step:

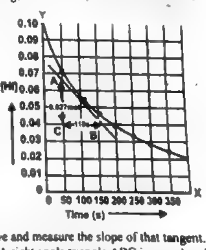
Ans.

Fast step	Rate determining step
(i) A step in a chemical reaction which proceeds so fastly that we are unable to determine the rate of reaction is called fast step.	A slowest step in reaction mechanism which can determine the overall rate of reaction is called rate determining step.
(ii) e.g., for a reaction $2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$ the steps of reaction mechanisms are (a) $2NO_{(g)} + H_2 \xrightarrow{slow} H_2O_{2(g)} + N_{2(g)}$ (b) $H_{2(g)} + H_2O_{2(g)} \xrightarrow{fast} 2H_2O_{(g)}$ (b) step is fast step.	(a) step is the rate determining step. It involves 2 moles NO and one mole H_2. $2NO_{(g)} + H_{2(g)} \xrightarrow{slow} H_2O_{2(g)} + N_{2(g)}$
(iii) Reactants of fast step are eliminated from rate equation.	Reactants of slow step are present in rate equation i.e., Rate = $k[H_2][NO_2]^2$
(iv) Not able to determine order of reaction.	Sum of reactant coefficients of slowest step is the order of reaction. Order of reaction = 2 + 1 = 3

Determination of the rate of a chemical reaction

When the reaction goes on, the concentrations of reactants decrease and those of products increase, the rate of a reaction, therefore, is expressed in terms of the rates at which the concentrations change.

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t} = \frac{mol.dm^{-3}}{sec} = mol.dm^{-3}\,sec^{-1}$$



Measurement of rate from the graph

Rate of a chemical reaction always decreases with the passage of time during the progress of reaction. To determine the rate of a reaction for a given length of time, a graph is plotted between time on x-axis and concentration of reactant on y-axis whereby a curve is obtained as shown in fig.

Let us consider the decomposition of HI to H_2 and I_2 at 508°C. Table tells us that the change in concentration of HI for first 50 seconds is 0.0284 mole dm^{-3} but 300 to 350 sec, the decrease is 0.031 moles dm^{-3}. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

Rate of reaction from slope measurement

To calculate the rate of reaction, draw a tangent, at 100 seconds, on the curve and measure the slope of that tangent. The slope of the tangent is the rate of reaction at that point i.e., after 100 seconds. A right angle triangle ABC is completed with a tangent as hypotenuse. Fig. shows that in 110 sec, the change in concentration is 0.027 mole dm^{-3}, and hence the

$$\text{Slope or Rate} = \frac{0.027\ mole\ dm^{-3}}{110\ sec} = 2.5 \times 10^{-4}\ moles\ dm^{-3} sec^{-1}$$

Methods for rate measurement

There are two types of methods

1. Physical Methods
2. Chemical Methods

1. PHYSICAL METHODS

The rate of a reaction can be determined by following physical methods.

Concentration of HI (mol. dm^{-3})	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0338	250
0.0296	300
0.0265	350

(i) Spectrometry

This method is applicable if a reactant or product absorbs ultraviolet, visible or infrared radiation. The rate of reaction can be measured by measuring the amount of radiation absorbed

(ii) Electrical Conductivity Method

The rate of a reaction involving ions can be studied by electrical conductivity method. The conductivity of such a solution depends upon the rate of change of concentration of the reacting ions formed during the reaction. The conductivity will be proportional to the rate of change in the concentration of such ions.

(iii) Dilatometric Method

This method is useful for those reactions, which involve small volume changes in solutions. The volume change is directly proportional to the extent of reaction.

(iv) Refractrometric Method

This method is applicable to reactions in solutions where there are changes in refractive indices of the substance taking part in the chemical reaction.

(v) Optical Rotation Method

This method is applicable to only those reactions in which anyone of the reactants or products is optically active Optical active substances rotate the plane polarized light. The extent of rotation determines the concentration of optically substance If any of the species in the reaction mixture is optically active, then this method can be followed to find out the rate reaction

Polarimater

"This is the instrument which is used to measure the angle through which plane polarized light is rotated by the reacting mixture."

2. CHEMICAL METHODS

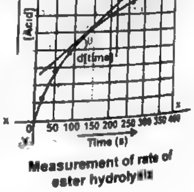
"The method which is used to analyse reactants or products chemically, is called chemical method."

In this method, the concentrations of reactants or products are measured by acid base titration, redox titration etc. at regular time intervals

For example

The hydrolysis of ethyl acetate in the presence of acid:

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \xrightarrow{H^+ (catalyst)} CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$



Measurement of rate of ester hydrolysis

The samples of reaction solution are withdrawn at regular time intervals and the amount of acetic acid produced at different time intervals is noted by acid base titration A graph is plotted between concentrations and time intervals. The different concentrations of acetic acid are plotted against the time whereby a curve is obtained. The slope of the curve at any point will give the rate of reaction. Initially the rate of reaction is high but it decreases with the passage of time. When the curve becomes horizontal, the rate becomes zero.

Energy of Activation

"The minimum amount of energy required for an effective collision is called energy of activation (E_a)."

Explanation

(i) During a chemical reaction, the particles of reactants must form a homogeneous mixture and collide with one another.

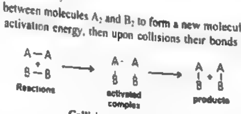
(ii) These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective, they give rise to the products otherwise the colliding particles just bounce back

(iii) The effective collisions can take place only when the colliding particles will possess certain amount of energy and they approach each other with the proper orientation The proper orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other

(iv) If all the collisions among the reacting species at a given temperature are effective in forming the products, the reaction is completed in a very short time Most of the reactions, are however, slow showing that all the collisions are not equally effective

Activated complex

Let us consider a reaction between molecules A_2 and B_2 to form a new molecule AB If these molecules will have energy equal to or more than the activation energy, then upon collisions their bonds will break and new bonds will be formed.



Collisions of molecules

Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short lived species and decomposes into products immediately. It has a transient existence that is why it is also called a transition state.

When the colliding molecules come close to each other at the time of collision, they slow down, collide and then fly apart. If the collision is effective then the molecules flying apart are chemically different otherwise the same molecules just bone back. When the molecules slow down just before the collision, their kinetic energy decreases and this results in the corresponding increase in their potential energy, the process can be understood with the help of a graph between the path of reaction and the potential energy of the reacting molecules.

The reactants reach the peak of the curve to form the activated complex. E_a is the energy of activation and it appears as a potential energy hill between the reactants and the products. Only, the colliding molecules with proper activation energy will be able to climb up the hill and give the products. If the combined initial kinetic energy of the reactants is less than E_a, they will be unable to reach the top of the hill and fall back chemically unchanged.

Activation energy for exothermic and endothermic reactions

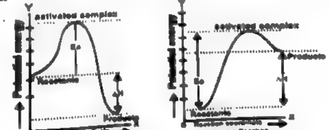
The potential energy diagram is used to study the heat evolved or absorbed during the reaction. The heat of reaction is equal to the difference in potential energy of the reactants and products.

Exothermic Reactions

For exothermic reactions, the products are at a lower energy level than the reactants and the decrease in potential energy appears as increase in kinetic energy of the products.

Endothermic Reactions

For endothermic reactions, the products are at higher energy level than the reactants and for such reactions a continuous source of energy is needed to complete the reaction.



A graph between path of reaction and the potential energy of the reaction

- The energy of activation of forward and backward reactions are different for all the reactions. For exothermic reactions, the energy of activation of forward reaction is less than that of backward reaction, while reverse in endothermic reactions.
- Energy of activation of a reaction provides valuable information about the way a reaction takes place and thus helps to understand the reaction.

Q7. (iv) Differentiate between enthalpy change of reaction and energy of activation of the reaction.

Ans.

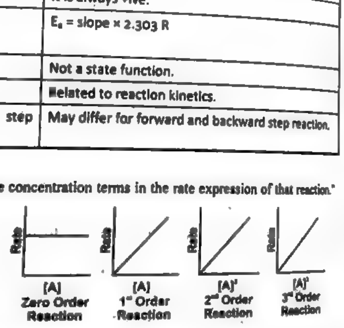
Enthalpy change	Energy of activation
(i) The amount of energy change (absorbed or evolved) during a chemical reaction at constant pressure is called enthalpy of reaction.	The minimum amount of energy which is required to form activated complex is called as activation energy. Minimum energy required to bring about an effective collection.
(ii) It is denoted by ΔH.	It is denoted by E_a.
(iii) It gives us the information about the energy difference between reactants and products.	It gives the information about path of reaction.
(iv) It may be +ive or –ive.	It is always +ive.
(v) $\Delta H = E + P\Delta V$ $\Delta H = q_p$	E_a = slope × 2.303 R
(vi) A state function.	Not a state function.
(vii) Related to thermo-chemistry.	Related to reaction kinetics.
(viii) Remains same for forward and backward step reaction.	May differ for forward and backward step reaction.

Finding the Order of Reaction

"The order of reaction is the sum of exponents of the concentration terms in the rate expression of that reaction."

It can be explained by the following methods:

1. Method of hit and trial
2. Graphical method
3. Differential method
4. Half life method
5. Method of large excess



Half life method

"Half life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction."

$$[t_{1/2}] \propto \frac{1}{a^{n-1}}$$

Let us perform a reaction twice by taking two different initial concentrations a_1 and a_2 and their half life periods are found to be t_1 and t_2 respectively.

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the above two equations:

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log on both sides, we have

$$\log\left(\frac{t_1}{t_2}\right) = \log\left[\left(\frac{a_2}{a_1}\right)^{n-1}\right]$$

$$\log\left(\frac{t_1}{t_2}\right) = (n-1)\log\left(\frac{a_2}{a_1}\right)$$

$$n = 1 + \frac{\log\frac{t_1}{t_2}}{\log\frac{a_2}{a_1}}$$

Method of large excess

One of the reactants is taken in a small amount as compared to the rest of the reactants. The active masses of the substances in large excess remain constant throughout. That substance controls the rate, which is taken in small amount and the order is noted with respect to that.

Factors Affecting Rate of Reaction

All those factors which change the number of effective collisions per second, affect the rate of a chemical reaction. Some of the important factors as follows:

1. Nature of reactants

The rate of reaction depends upon the nature of reacting substances and the chemical reactivity of the substances is controlled by the electronic arrangements in their outermost orbital.

- The element of IA group has one electron in their outermost s-orbital, and they react with water more swiftly than those of IIA group elements having two electrons in their outermost orbital. For example Ca reacts at a moderate rate while Na reacts with explosive violence.
- Most of the ionic reactions are very fast. Oxidation-reduction reactions involve the transfer of electrons and are slower than ionic reactions.

2. Concentration of reactants

The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will result in the corresponding increase in the reaction rate while a decrease in the concentrations will have a reverse effect.

Example (i)

Combustion that occurs slowly in air (21% oxygen) will occur more rapidly in pure oxygen.

Example (ii)

Lime stone reacts with different concentrations of HCl at different rates.

Example (iii)

Let us consider the following gaseous reaction:

$$2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$$

In this reaction, four moles of reactants form three moles of the products. So the pressure is decreased during the progress of reaction. The rate of reaction between NO and H_2 at 800°C are studied by changing in pressure.

Effect of Change in Concentrations of Reactants on the Rate of Reaction

Experiment Number	NO (moles dm^{-3})	H_2 (moles dm^{-3})	Initial rate ($atm.min^{-1}$)
1	0.006	0.001	0.025
2	0.006	0.002	0.050
3	0.006	0.003	0.075
4	0.001	0.009	0.0063
5	0.002	0.009	0.025
6	0.003	0.009	0.056

Table shows the results of six experiments. In the first three experiments the concentration of H_2 is increased by keeping the concentration of NO constant. By doubling the concentration of H_2, the rate is doubled and by tripling the concentration of H_2, the rate is tripled. So, the rate of reaction is directly proportional to the first power of concentration of H_2.

$$\text{Rate} \propto [H_2]$$

In the next three experiments, the concentration of H_2 is kept constant. By doubling the concentration of NO, the rate increases four times and by tripling the concentration of NO the rate is increased nine times. So, the rate is proportional to the square of concentration of NO.

$$\text{Rate} \propto [NO]^2$$

Combining above two rate expressions:

$$\text{Rate} \propto [H_2][NO]^2$$

$$\text{Rate} = k[H_2][NO]^2$$

Hence, the reaction is a third order one. The proposed mechanism is

$$2NO_{(g)} + H_{2(g)} \xrightarrow{\text{Slow}} N_{2(g)} + H_2O_{2(g)}$$

$$H_2O_{2(g)} + H_{2(g)} \xrightarrow{\text{Fast}} 2H_2O_{(g)}$$

$$\text{Rate} = k[NO]^2[H_2]$$

3. Surface area

The increased surface area of reactants, increase the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance.

Example (i): Aluminium foil reacts with NaOH moderately when warmed but powdered Al reacts rapidly with cold NaOH and H_2 gas is evolved.

$$2Al + 2NaOH + 6H_2O \longrightarrow 2NaAl(OH)_4 + 3H_2$$

Example (ii): $CaCO_3$ in the powder form reacts with dilute H_2SO_4 more quickly than its big pieces.

4. Light

Light consists of photons having definite amount of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates of reactions are enhanced.

Examples

(i) The reaction of CH_4 and Cl_2 requires light.

$$CH_4 + Cl_2 \xrightarrow{\text{Sunlight}} CH_3Cl + HCl$$

(ii) The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in day-light but explosive in sunlight.

(iii) Light plays a vital role in photosynthesis.

(iv) Photography is one of the best aspects of chemical reactions which are light sensitive.

(v) The halides of silver metal are sensitive to light.

5. Effect of temperature on the rate of reaction

- The collision theory of a reaction rates given us that the rate of a reaction is proportional to the number of collisions among the reactant molecules.
- Anything that can increase the frequency of collisions should increase the rate.
- For a collision to be effective the molecules must to possess the activation energy and they must also be properly oriented.
- For nearly all chemical reactions, the activation energy is quite large and at ordinary temperature very few molecules are moving fast enough to have this minimum energy.
- All the molecules of a reactant do not possess the same energy at a particular temperature.
- Most of the molecules will possess average energy.

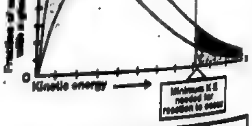


Fig: Kinetic energy distributions for a reaction mixture at two different temperatures. The size of the shaded areas under the curves are proportional to the total fraction of molecules that possess the minimum activation energy.

- A fraction of total molecules will have energy more than the average energy. This fraction of molecules is indicated as shaded as shown in fig.
- As the temperature increases, the number of molecules in this fraction also increases.
- So the number of effective collision increases and hence the rate increases.
- When the temperature of reacting gases is raised by 10 K, the fraction of molecule with energy more than E_a roughly doubles and so the reaction rate also doubles.

Increasing the temperature does not change the activation energy or the total number of molecules the shape of the curve changes.

A greater proportion of molecules exceeds the activation energy at higher temperature

Arrhenius Equation

The effect of temperature on rate of reaction is explained on the basis of Arrhenius equation. The rate constant 'k' for many simple reaction is found to vary with temperature. According to Arrhenius:

$$k = Ae^{-E_a/RT}$$

- k is exponentially related to activation energy E_a and temperature T. R is a general gas constant and e is the base of logarithm.
- The equation shows that the increase in temperature, increase the rate constant and the reaction of high activation energy have low "k" values.
- The factor "A" is called Arrhenius constant and it depends upon the collision frequency of the reacting substances.
- The equation helps us to determine the energy of activation of the reaction as well.
- For this purpose, we take natural log of Arrhenius equation:

$$\ln(k) = \ln(Ae^{-E_a/RT}) \quad \text{.....(1)}$$

$$\ln k = \ln A + \ln e^{-E_a/RT}$$

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right)\ln e$$

Since $\ln e = 1$ (log of a quantity with same base is unity)

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \text{......(2)}$$

The equation (2) is the equation of straight line, and from the slope of straight line 'E_a' can be calculated. In order to convert this natural log into common log of base 10, we multiply the *ln* term with 2.303

$$2.303 \log k = -\frac{E_a}{RT} + 2.303 \log A \quad \text{(The base of common log is 10)}$$

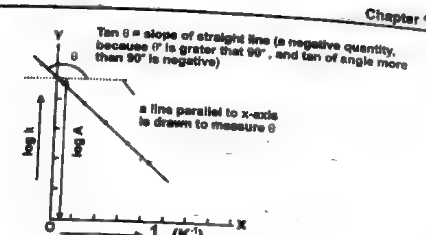
Dividing the whole equation by 2.303

or
$$\log k = -\frac{E_a}{2.303RT} + \log A \quad \text{......(3)}$$

The equation (3) is again the equation of straight line resembling

$$y = -mx + c$$

Where 'm' in is slope of straight line and 'c' is the intercept of straight line. Temperature is independent variable in this equation while rate constant k is dependent variable. The other factors like E_a, R and A are constants for a given reaction.



Arrhenuis plot to calculate the energy of activation

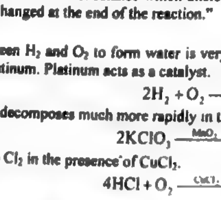
When a graph is plotted between 1/T on x-axis and log k on y-axis, a straight line is obtained with a negative slope. The slope of the straight line is measured by taking tangent of that angle θ which this straight line makes with the x-axis. This slope is equal to $-\frac{E_a}{2.303R}$

$$Slope=\frac{-E_a}{2.303R}$$

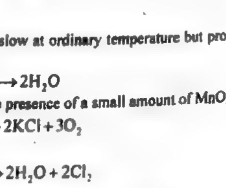
$$E_a=-Slope\times 2.303R$$

The straight lines of different reactions will have different slopes and different "Ea" values. The unit of slope are in Kelvins (K).

$$Slope=\frac{J\,mol^{-1}}{2.303Jk^{-1}\,mol^{-1}}=K$$



Arrhenius plot for decomposition of N_2O_5



Potential energy diagram of N_2O_5 decomposition

CATALYST

"A catalyst is defined as a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction."

Examples

1. The reaction between H_2 and O_2 to form water is very slow at ordinary temperature but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst.

$$2H_2+O_2\xrightarrow{Pt}2H_2O$$

2. Similarly, $KClO_3$ decomposes much more rapidly in the presence of a small amount of MnO_2.

$$2KClO_3\xrightarrow{MnO_2}2KCl+3O_2$$

3. HCl is oxidized to Cl_2 in the presence of $CuCl_2$.

$$4HCl+O_2\xrightarrow{CuCl_2}2H_2O+2Cl_2$$

CATALYSIS

"The process, which takes place in the presence of a catalyst, is called catalysis."

Types of catalysis

(a) Homogeneous Catalysis
(b) Heterogeneous Catalysis

(a) Homogeneous Catalysis

"When the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout, then it is called homogeneous catalysis."

The catalyst is distributed uniformly throughout the system.

Examples

(i) The formation of SO_3 from SO_2 and O_2 in the lead chamber process for the manufacture of sulphuric acid needs NO as a catalyst. Both the reactants and the catalyst are gases.

$$2SO_{2(g)}+O_{2(g)}\xrightleftharpoons{NO_{(g)}}2SO_{3(g)}$$

(ii) Esters are hydrolyzed in the presence of H_2SO_4. Both the reactants and the catalyst are in the solution state

$$CH_3COOC_2H_{5(aq)}+H_2O_{(l)}\xrightleftharpoons[H_2SO_4]{H_3O^+}CH_3COOH_{(aq)}+C_2H_5OH_{(aq)}$$

(b) Heterogeneous Catalysis

"When the catalyst and the reactants are in different phases, then it is called heterogeneous catalysis."

Examples

(i) Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3

$$4NH_{3(g)}+5O_{2(g)}\xrightleftharpoons{Pt_{(s)}}4NO_{(g)}+6H_2O_{(g)}$$

(ii) Hydrogenation of unsaturated organic compounds are catalysed by finely divided Ni

$$CH_2{=}CH_{2(g)}+H_{2(g)}\xrightleftharpoons{Ni_{(s)}}CH_3{-}CH_{3(g)}$$

(iii) Manufacture of H_2SO_4 by contact process needs $V_2O_{5(s)}$ catalyst for the combination of $SO_{2(g)}$ and $O_{2(g)}$

$$2SO_{2(g)}+O_{2(g)}\xrightleftharpoons{V_2O_{5(s)}}2SO_{3(g)}$$

(iv) The reaction of H_2 and N_2 in the presence of finely divided iron is a well known Haber's process for the manufacture of NH_3.

$$N_{2(g)}+3H_{2(g)}\xrightleftharpoons{Fe_2O_{3(s)}}2NH_{3(g)}$$

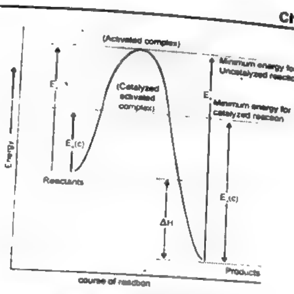
Q7. (ii) Differentiate between homogeneous and heterogeneous catalyses.

Ans.

	Homogeneous Catalysis	Heterogeneous Catalysis
(i)	It is catalysis in which the catalyst and reacting substances are in same physical state/phase.	It is catalysis in which the catalyst and reacting substances are in different phases
(ii)	Catalyst is uniformly distributed	No uniform distribution of catalyst.
(iii)	Mostly liquid or gaseous catalysts are used in homogeneous catalysis.	Catalyst is solid and reacting substances are either liquids or gases.
(iv)	e.g., $2SO_{2(g)}+O_{2(g)}\xrightleftharpoons{NO_{(g)}}2SO_{3(g)}$	$4NH_{3(g)}+5O_{2(g)}\xrightleftharpoons{Pt_{(s)}}4NO_{(g)}+6H_2O_{(g)}$

Catalysis and energy of activation

A catalyst increases the reaction rate by decreasing the energy of activation of a reaction. A new reaction path is provided to the reaction. In this way greater number of molecules can cross the lower energy barrier as shown in fig



Catalyzed and uncatalyzed reactions

CHARACTERISTICS OF A CATALYST

1. Unchanged chemical composition

A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state

Examples

(i) MnO_2 is added as a catalyst for the decomposition of $KClO_3$. But MnO_2 is regenerated at the end in the form of a fine powder

(ii) In some cases, the shining surfaces of the solid catalyst become dull.

2. Effectiveness of a catalyst

Sometimes, we used a trace of a metal catalyst to effect very large amount of reactants.

Examples

(i) 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.

(ii) Dry HCl and NH_3 don't combine, but in the presence of trace of moisture, they give dense white fumes of NH_4Cl

(iii) Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.

3. Surface area

A catalyst is more affective when it is present in a finely divided form.

Examples

(i) A lump of platinum will have much less catalytic activity than colloidal platinum.

(ii) A finely divided nickel is used for the hydrogenation of vegetable oils.

4. Equilibrium position remains unaffected

A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.

5. Thermo-dynamical condition

A catalyst cannot start a reaction, which is not thermodynamically feasible. The mechanism of a catalysed reaction is different from that of an uncatalysed reaction.

6. One reaction one catalyst

[illegible] is specific in its action. When a particular catalyst works for one reaction it may not necessarily work [illegible]. If different catalysts are used for the some reactant then the products may change.

Examples

[illegible] the presence of Al_2O_3 but gives H_2 and CO_2 in the presence of Cu metal

$$HCOOH \xrightarrow{Al_2O_3} H_2O + CO$$

$$HCOOH \xrightarrow{Cu} H_2 + CO_2$$

(ii) Ethyl alcohol gives ethane when passed over hot aluminium oxide but with hot copper it gives acetaldehyde

$$C_2H_5OH \xrightarrow{Al_2O_3} C_2H_4 + H_2O \text{ (Dehydration of alcohol)}$$

$$C_2H_5OH \xrightarrow{Cu} CH_3CHO + H_2 \text{ (Dehydrogenation of alcohol)}$$

7. Temperature affects the role of catalyst

Some catalysts are physically altered by a change in temperature and hence their catalytic power will be decreased.

Example

Colloidal catalysts like platinum may be coagulated with the rise in temperature

8. Catalytic poisoning

The presence of some amount of foreign substances which render them ineffective. Such substances are called poisons.

The poisoning of a catalyst may be temporary or permanent. In permanent poisoning, the poison [illegible] chemically with the catalyst

Example

(i) The decomposition of H_2O_2 is catalysed by colloidal platinum. It can be rendered ineffective by traces of HCN.

(ii) The presence of CO as an impurity with hydrogen decreases the catalytic activity of catalyst in the Haber's process for the manufacture of NH_3.

(iii) The manufacture of H_2SO_4 in the contact process needs platinum as a catalyst. The traces of arsenic present as impurities in the reacting gases make platinum ineffective. That is why arsenic purifier is used in the contact process.

Activation of catalyst

"A substance which promotes the activity of a catalyst is called a promoter or activator. It is also called "catalyst for a catalyst."

Examples

(i) Hydrogenation of vegetable oils is accelerated by nickel. The catalytic activity of nickel can be increased by using copper and tellurium.

(ii) In Haber's process for the manufacture of ammonia, iron is used as catalyst. If small amounts of some high melting oxides like aluminium oxide, chromium oxide or rare earth oxides are added they increase the efficiency of iron

Negative catalysis

"When the rate of reaction is retarded by adding a substance, then it is called to be a negative catalyst or inhibitor."

Example

Tetraethyl lead is added to petrol, because it saves the petrol from pre-ignition

Auto-catalyst

"The substance which is formed in the course of reaction sometime acts as catalyst."

Examples

(i) Hydrolysis of ethyl acetate generates acetic acid, which acts as a catalyst for further reaction

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

(ii) When copper is allowed to react with nitric acid, the reaction is slow in the beginning. It gains the speed gradually and finally become very fast. This is due to the formation of nitrous acid during the reaction, which accelerates the process.

(iii) The reaction of oxalic acid with acidified $KMnO_4$ is slow at the beginning but after sometime $MnSO_4$ produced in the reaction makes it faster.

Enzyme catalysis

"Enzymes are the complex protein molecules and catalyze the organic reactions in the living cells."

Many enzymes have been identified and obtained in the pure crystalline state. The first enzyme was prepared in the laboratory in 1969.

Examples

(a) Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soyabean.

$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{Urease} 2NH_3 + CO_2$$

(b) Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called invertase, present in the yeast.

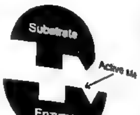
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$

(c) Glucose is converted into ethanol by the enzyme zymase present in the yeast.

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$

Mode of enzyme action

Enzymes have active centres on their surfaces. The molecules of a substrate fit into their activities just as a key fits into a lock. The substrate molecule enters the cavities form complex, reacts and the product get out of the cavity immediately.



Lock and Key mode of enzyme catalysis

In 1913, Lenor Michaels and his student, M.L. Menton, studied the mechanism of enzyme catalysis.

$$E + S \rightleftharpoons ES \longrightarrow P + E$$

Where E = Enzyme S = Substrate (reactant)

ES = Activated complex, P = product

Characteristics of enzymes catalysis

The enzyme act as catalysts like inorganic heterogeneous catalysts. They are unique in their efficiency and have a high degree of specificity.

(a) Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.

(b) Enzyme catalysis is highly specific, for example, urease catalyses the hydrolysis of urea only and it cannot hydrolyze any other amide even methyl urea.

(c) Enzyme catalytic reactions have the maximum rates at on optimum temperature.

(d) The pH of the medium also controls the rates of the enzyme catalyzed reactions and the rate passes through maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.

(e) The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme.

KEY POINTS

1. The studies concerned with rates of chemical reactions and factors that affect the rates of chemical reactions and the mechanism of reactions constitute the subject matter of reaction kinetics.
2. The rate of a reaction is the change in the concentration of a reactant or a product divided by the time taken for the reaction. The rate of reaction between two specific time intervals is called the average rate of reaction. While the rate at any one instant during the interval is called the instantaneous rate. Rate constant of a chemical reaction is rate of reaction when the concentrations of reactants are unity.
3. Order of reaction is the sum of exponents of the concentration terms in the rate expression of a chemical reaction. The exponents in the expression may or may not be different from the coefficients of the chemical equation. Order of a reaction may be zero, whole number of fractional.
4. Half-life period of a reaction is the time required to covert 50% of the reactants into products. Half-life period of an any reaction is inversely proportional to the initial concentration raised to the power one less than the order of that reaction.
5. The step which limits how fast the overall reaction can proceed is known as the rate determining step.

6. Determination of the rate of a chemical reaction involves the measurement of the concentration of reactants or products at regular time intervals during the progress of reaction. The change in concentration of reactants and products can be determined by both physical and chemical methods.
7. The effective collisions between the colliding species will take place only when the reactant molecules possess minimum amount of energy, which is called the energy of activation. Moreover, proper orientation is also necessary.
8. All those factors, which change the number of effective collisions per second, affect the rate of chemical reaction. Some of the important factors are, nature and concentration of reactants, surface area, light, and temperature and catalyst.
9. A catalyst is a substance, which alters the rate of a chemical reaction, but itself remains chemically unchanged at the end of reaction. The process when the catalyst and the reactants are in the same phase is said to be a homogenous catalysis. In case of heterogeneous catalysis, the catalyst and the reactants are in different phases. A substance, which promotes the activity of a catalyst, is called promoter or activator. In certain reactions, a product formed acts as a catalyst, the phenomenon is called auto-catalysis.
10. Enzymes are the complex protein molecules, which catalyze the reactions in the living cells.

SOLVED OBJECTIVE EXERCISE

Q1. Multiple choice questions:

(i) In a zero order reaction, the rate is independent of:
(a) temperature of reaction (b) concentration of reactants
(c) concentration of products (d) None of these

(ii) If the rate equation of a reaction $2A + B \longrightarrow$ product is rate $= k[A]^2[B]$ and A is present in large excess, then order of reaction is
(a) 1 (b) 2
(c) 3 (d) None of these

(iii) The rate of reaction:
(a) increases as the reaction proceeds
(b) decreases as the reaction proceeds
(c) remains the same as the reaction proceeds
(d) may decrease or increase as the reaction proceeds

(iv) With the increase of 10°C temperature the rate of reaction doubled. This increase is due to:
(a) decrease in activation energy of reaction
(b) decrease in number of collisions between molecules
(c) increase in activation energy of reactants.
(d) increase the number of effective collisions

(v) The unit of rate constant is the same as that of rate of reaction in:
(a) first order reaction (b) second order reaction
(c) zero order reaction (d) third order reaction

Solved Exercise MCQ's

Q. No	Answer	Reason
(i)	(b) concentration of reactants	"The reaction which is entirely independent of the concentration of reactant molecules is called zero order reaction." Rate = $k[A]^0$
(ii)	(a) 1	When the reactant is in excess its concentration does not effect the rate of reaction so the above reaction is first order reaction.

(iii)	(b) decreases as the reaction proceeds	The rate of reaction is directly proportional to concentration of reactant As reaction goes the amount of reactant decrease hens the rate of reaction decreases
(iv)	(d) increase the number of effective collisions	Every factor which effects the number of effective collisions effect the rate of reaction.
(v)	(c) zero order reaction	$A \longrightarrow$ Product Rate $= k[A]^0$ So, Rate $= k =$ moldm^{-3} s^{-1}

Q2. Fill in the blanks:

(i) The rate of an endothermic reaction ________ with increase in temperature.

(ii) All radioactive disintegration nuclear reactions are of ________ order.

(iii) For a fast reaction, the rate constant is relatively ________ and half life is ________.

(iv) The second order reaction becomes ________ if one of the reactants is taken in large excess.

(v) Arrhenius equation can be used to find out ________ of a reaction

ANSWERS

(i) increases	(ii) first
(iii) large, small	(iv) Pseudo first
(v) energy of activation	

Q3. Indicate true or false:

(i) The half life of a first order reaction increases with temperature.

(ii) The reactions having zero activation energy are instantaneous.

(iii) A catalyst makes a reaction more exothermic.

(iv) There is a difference between rate law and law of mass action.

(v) The order of reaction is strictly determined by the stoichiometry of balanced chemical equation.

ANSWERS

(i) False	(ii) True	(iii) False	(iv) False	(v) False

SHORT ANSWERS TO EXERCISE

Q16. Define the following terms with examples.

(i) Homogeneous catalysis:

Ans. The catalysis in which the catalyst and the reactants are in the same phase is called homogeneous catalysis

e.g.,

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO_{(g)}} 2SO_{3(g)}$$

(ii) Heterogeneous catalysis:

Ans. The catalysis in which the catalyst and the reactants are in different phases, is called heterogeneous catalysis

e.g.,

1. $CH_2 = CH_2 + H_2 \xrightleftharpoons{Ni_{(s)}} CH_3 - CH_3$

2. $4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt_{(s)}} 4NO_{(g)} + 6H_2O_{(g)}$

(iii) Activation of a catalyst:

Ans. The phenomenon in which the catalytic activity of the catalyst is enhanced The substance added is called **promotor, activator or catalyst for a catalyst.**

e.g.,

$$N_2 + 3H_2 \xrightleftharpoons[(Al_2O_3,\ MgO)\ Cr_2O_3\ \text{promotor}]{Fe(\text{catalyst})} 2NH_3$$

$$\underset{(\text{ethene})}{C_2H_4} + H_2 \xrightarrow[Cu/Te\ (\text{Promoter})]{Ni\ (\text{catalyst})} \underset{(\text{ethane})}{C_2H_6}$$

(iv) Autocatalyst:

Ans. A substance which is produced in a chemical reaction and acts as a catalyst is called autocatalyst e.g., in the following reaction.

$$5(COOH)_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + \boxed{2MnSO_4} + 10CO_2 + 8H_2O$$

$MnSO_4$ is an autocatalyst.

(v) Catalytic poisoning:

Ans. The decrease in the efficiency of a catalyst or catalytic activity of a catalyst is called catalytic poisoning of catalyst and the substance which brings about this, is called a poison or inhibitor

e.g., During the manufacture of H_2SO_4 by contact process, V_2O_5 is used as a catalyst in contact tower to produce SO_3

$$2SO_2 + O_2 \xrightleftharpoons[V_2O_5\ (s)]{} 2SO_3$$

Arsenic is a poison to this catalyst

(vi) Enzyme catalysis:

Ans. The catalysis in which an enzyme acts as a catalyst is called enzyme catalysis Enzymes are complex protein molecules in nature and increase the rate of metabolic reaction in the living organisms.

e.g., hydrolysis of urea is done by urease.

$$NH_2-\overset{\overset{O}{||}}{C}-NH_2 + H_2O \xrightleftharpoons{\text{Urease}} 2NH_3 + CO_2$$

(vii) Specific rate constant:

Ans. It is equal to the rate of reaction when the concentration of reacting substances are taken as unity

Consider a reaction

$$aA + bB \longrightarrow \text{Product}$$

Rate of reaction $\propto [A]^a[B]^b$

Rate of reaction $= k[A]^a[B]^b$

If $[A]^a = [B]^b = 1$ then

Rate of reaction $= k$

K is called specific rate constant or velocity constant of reaction.

Q17. Briefly describe the following with example:

(i) Change of physical state of a catalyst at the end of reaction.

Ans. A catalyst remains unchanged in mass and chemical composition at the end of a chemical reaction but its physical appearance may change.

(a) e.g., $2KClO_3 \xrightarrow[(MnO_2)]{} 2KCl + 3O_2$

MnO_2 is used in the form of granules for the decomposition of $KClO_3$ to produce O_2. At the end of reaction, it will be converted into powder.

(b) Reaction where metallic catalysts are used, at the end of reaction surface of metal can be tarnished (loss of luster).

(ii) A very small amount of a catalyst may prove sufficient to carry out a reaction.

Ans. A catalyst is always added in trace amount to speed up a chemical reaction. e.g.,

(a) 1g of colloidal Pt can decompose thousands of dm^3 of H_2O_2.

$$2H_2O_2 \xrightarrow{Pt} 2H_2O + O_2$$

(b) Dry HCl and dry NH_3 do not combine with each other but a trace amount of moisture give dense fumes of NH_4Cl

$$NH_3 + HCl \xrightarrow{H_2O} NH_4Cl$$

(c) 1 mg of powdered Pt can convert 2.5 dm^3 of H_2 and 1.25 dm^3 O_2 into water.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

(iii) A finely divided catalyst may prove more effective.

Ans. A finely divided catalyst has increased surface area. Thus rate of reaction is increased as compared to a reaction where a foil, sheet or compact form of catalyst is used.

e.g.

(a) Lump of Pt has less catalytic activity than colloidal Pt.

(b) Finely divided Ni is used in hydrogenation of vegetable oil than a foil of Ni.

(iv) Equilibrium constant of a reversible reaction is not changed in the presence of catalyst.

Ans. Consider a reversible reaction

$$A + B \rightleftharpoons C + D$$

Its equilibrium constant can be written as

$$K_C = \frac{[C][D]}{[A][B]}$$

Most of the equilibrium reactions are slow so an appropriate catalyst is added which increases the rates of both forward and backward reactions to establish the equilibrium earlier. A catalyst decreases activation energy. As no effect is observed for K_c or its position. Therefore addition of catalyst does not effect the K_c of reaction.

(v) A catalyst is specific in action.

Ans. It means that a particular catalyst works for one reaction.

It may not necessarily work for any other reaction.

If different catalysts are used for the same reaction, then products may change.

e.g., reaction for decomposition of formic acid.

(a) $HCOOH \xrightarrow{Al_2O_3} H_2O + CO$

(b) $HCOOH \xrightarrow{Cu} H_2 + CO_2$

A catalyst suitable for a forward reaction, may be used to carry out a back reaction in reversible reactions e.g.

$$NH_2-\overset{\overset{O}{||}}{C}-NH_2 + H_2O \underset{}{\overset{Urease}{\rightleftharpoons}} 2NH_3 + CO_2$$

NUMERICAL OF EXERCISE

Q19. In the reaction of NO and H_2 it was observed that equimolar mixture of gases at 340.5 mm of Hg pressure was half changed in 102 seconds. In another experiment with an initial pressure of 288 mm of Hg the reaction half completed in 140 second. Calculate order of reaction.

Given data:

(i) For first experiment
Initial concentration = a_1 = 340.5 mm of Hg
Half life = t_1 = 102 second

(ii) For 2nd experiment
Initial concentration = a_2 = 288 mm of Hg
Half life = t_2 = 140 sec

Requirement:

n = order of reaction = ?

Solution:

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

$$= 1 + \frac{\log\left[\frac{102}{140}\right]}{\log\left[\frac{288}{340.5}\right]}$$

$$n = 1 + \frac{\log[0.7286]}{\log[0.8471]}$$

$$n = 1 + \frac{(-0.1375)}{(-0.0721)}$$

$$n = 1 + 1.907$$

$$n = 2.907 \cong 3$$

Answer: Order of reaction = 3

Q20. A study of chemical kinetics of a reaction

$$A + B \longrightarrow \text{Products}$$

gave the data at 25°C. Calculate the rate law.

	[A]	[B]	Rate
Experiment 1	1.00	0.15	4.2×10^{-6}
Experiment 2	2.00	0.15	8.4×10^{-6}
Experiment 3	1.00	0.2	5.6×10^{-6}

1st Method: Theoretical

Rate of a chemical reaction can be altered by changing the conc. of [A] or [B].

In experiment 1 and experiment conc. of [B] is same while that of conc. of [A] is doubled.

It is observed that rate of reaction also doubles by doubling the concentration of [A] so

Rate $\propto [A]^1$ (with respect to [A])

In experiment 1 and experiment 3, conc. of [A] is same but conc. of [B] is altered. It is observed that by increasing the reactant [B] the rate increases to same extent so

Rate $\propto [B]^1$ (with respect to [B])

The overall rate of reaction is

$$\text{Rate} \propto [A]^1[B]^1$$

Order of reaction is sum of exponents of [A] and [B] = 1 + 1 = 2.

Answer: Rate equation is

$$\text{Rate} \propto [A]^1[B]^1$$

Order of reaction is = 2

2nd Method: Calculation

Order of a reaction can be calculated with respect to a reactant by a formula.

$$\frac{\text{conc. of reactant in experiment 2}}{\text{conc. of reactant in experiment 1}} = \frac{\text{rate of experiment 2}}{\text{rate of experiment1}}$$

Order of reaction with respect to A:

We can compare experiment 2 and experiment 1.

Given data:

conc. of reactant A in experiment 2 = 2 mol

conc. of reactant A in experiment 1 = 1 mol

Rate in experiment 1 = 4.2×10^{-6}

Rate in experiment 2 = 8.4×10^{-6}

Requirement:

Order of reaction with respect to [A] = ?

Solution:

$$\frac{2}{1} = \frac{8.4\times10^{-6}}{4.2\times10^{-6}}$$

$$2 = 2$$

Means by doubling the conc. of reactant [A] rate becomes doubles so Rate $\propto [A]^1$.

Order of reaction with respect to B:

We can compare experiment 1 and experiment 3.

Given data:

conc. of reactant B in experiment 1 = 0.15 mol

conc. of reactant B in experiment 2 = 0.2 mol

Rate of reactant in experiment 1 = 4.2×10^{-6}

Rate of reaction in experiment 3 = 5.6×10^{-6}

Requirement:

Rate of reaction with respect to [B] = ?

Solution:

$$\frac{0.2}{0.15} = \frac{5.6\times10^{-6}}{4.2\times10^{-6}}$$

$$1.33 : 1.33$$

It means rate of reaction increases in a same proportion as [B] increases so

$$\text{Rate} \propto [B]^1$$

Overall rate:

$$\text{Rate} \propto [A]^1[B]^1$$

Order of reaction:

$$1 + 1 = 2$$

Q21. Some reactions taking place around room temperature have E_a around 50 kJ mol^{-1}.

(i) What is the value of factor $e^{-Ea/RT}$ at 25°C.

(ii) Calculate the same value at 35° and 45°C.

(iii) Prove that for every 10°C rise in temperature, the factor gets doubled so rate also doubles.

(i) Data:

E_a = 50 kJ mol^{-1} = 50000 J mol^{-1}

T = 25°C + 273 = 298 K

R = 8.313 J K^{-1} mol^{-1}

Requirement:

$e^{-Ea/RT}$ = ?

Solution:

$$\frac{Ea}{RT} = \frac{50000}{298\times8.313} = 20.183$$

$$= e^{-20.183}$$

$$= 1.71 \times 10^{-9}$$

Answer: $e^{-Ea/RT} = 1.71\times10^{-9}$

(ii) (a) Given data:

Ea = 50 kJ mol^{-1} = 50000 J mol^{-1}

T = 35°C + 273 = 308 K

R = 8.313 J mol^{-1} K^{-1}

Requirement:

$e^{-Ea/RT}$ = ?

Solution:

$$\frac{Ea}{RT} = \frac{50000}{8.313\times308}$$

$$= 19.52$$

$$e^{-Ea/RT} = e^{-19.52} = 3.31 \times 10^{-9}$$

Answer: $e^{-Ea/RT} = 3.31\times10^{-9}$

(b) Given data:

E_a = 50 kJ mol^{-1} = 5000 J mol^{-1}

T = 45°C + 273 = 318 K

R = 8.313 J mol^{-1} K^{-1}

Requirement:

$e^{-Ea/RT}$ = ?

Solution:

$$\frac{Ea}{RT} = \frac{50000}{318\times8.313} = 18.914$$

$$e^{-Ea/RT} = e^{-18.914} = 6.1 \times 10^{-9}$$

Answer: $e^{-Ea/RT} = 6.1\times10^{-9}$

(iii) Comparison of value of $e^{-Ea/RT}$ at 25°, 35° and 45°C.

Given data:

at 25°C, $e^{-Ea/RT} = 1.71 \times 10^{-9} = e_1$

at 35°C, $e^{-Ea/RT} = 3.31 \times 10^{-9} = e_2$

at 45°C, $e^{-Ea/RT} = 6.1 \times 10^{-9} = e_3$

Requirement:

Comparison of e_1 and e_2 = ?

Comparison of e_2 and e_3 = ?

Solution:

For comparison take the ratios of $\frac{e_2}{e_1}$ and $\frac{e_3}{e_2}$

(a) $\frac{e_2}{e_1} = \frac{3.31 \times 10^{-9}}{1.71 \times 10^{-9}} = 1.93 \cong 2$

means $e_2 > e_1$ by a factor 2.

(b) $\frac{e_3}{e_2} = \frac{6.1 \times 10^{-9}}{3.31 \times 10^{-9}} = 1.84 \cong 2$

means $e_3 > e_2$ by a factor 2.

Proof:

Value of $e^{-Ea/RT}$ at 45°C is double than that at 35°C. This value is in turn double than value at 25°C.

Conclusion:

As according to Arrhenius equation $K = A.e^{-Ea/RT}$, Rate of reaction also become double by a 10°C rise in temperature.

Q22. **H_2 and I_2 react to produce HI. Following data for rate constant at various temperatures have been collected.**

Temp (K)	Rate constant (K) ($cm^3\ mol^{-1}\ s^{-1}$)
500	6.814×10^{-4}
550	2.64×10^{-2}
600	0.56×10^{0}
650	7.31×10^{0}
700	66.67×10^{0}

(i) **Plot a graph between l/T and log K.**

(ii) **Measure the slope of straight line and calculate the energy of activation for this reaction.**

Ans. **(i) To plot a graph between 1/T and log K the given data is converted into these values.**

T	$1/T\ K^{-1}$	k	log k
500 K	$2 \times 10^{-3} = 0.002$	6.814×10^{-4}	−3.16
550 K	$1.81 \times 10^{-3} = 0.0018$	2.64×10^{-2}	−1.58
600 K	$1.66 \times 10^{-3} = 0.0016$	0.56×10^{0}	−0.25
650 K	$1.53 \times 10^{-3} = 0.0015$	7.31×10^{0}	0.86
700 K	$1.42 \times 10^{-3} = 0.0014$	66.67×10^{0}	1.82

To plot a graph 1/T is taken on x-axis and log k is taken on y-axis.

Scale of graph:

x-axis: A big square = $0.002\ K^{-1}$

y-axis: A big square = 1 whole number

(ii) **Finding slope and E_a**

To find the slope from graph we can calculate base and perpendicular by subtracting initial values from final values.

(a) For base:

Initial l/T = 0.002

Final l/T = 0.0014

Difference = 0.0014 − 0.002

= −0.0006

(b) For perpendicular:

Initial log K = −3.16

Final log K = 1.82

Difference = 1.82 − (−3.16)

= 4.98

$$\text{Slope} = \text{Hypotenuse} = \frac{\text{Perpendicular}}{\text{Base}}$$

$$= \frac{4.98}{-0.0006}$$

$= -8300\ K$

$E_a = -\text{Slope} \times 2.303\ R$

$= -(-8300) \times 2.303(8.313)$

$= 158902.1637\ \text{Joules mol}^{-1}$

$E_a = 158.9\ \text{kJ mol}^{-1}$

SOLVED EXAMPLES

Example (1):

Calculate the half life period of the following reaction when the initial concentration of HI is 0.05M.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

The value of rate constant $K = 0.079 dm^3\ mole^{-1}\ sec^{-1}$ at 508 °C and rate of expression is

Rate = $K[HI]^2$

Ans. **Given Data:**

Initial concentration of HI = 0.05M

Rate constant = k = $0.079\ dm^3\ mole^{-1}\ sec^{-1}$

Required:

Half life period = $[t_{1/2}]_2$ = ?

Solution:

According to equation it is second order reaction. The half life period of second order reaction is

$$[t_{1/2}]_2 = \frac{1}{ka^{2-1}} = \frac{1}{ka}$$

Putting the values of k and a

So,

$$[t_{1/2}]_2 = \frac{1}{k \times a}$$

$$= \frac{1}{(0.079 dm^3 mol^{-1} sec^{-1})(0.050 mol dm^{-3})}$$

$$= \frac{1}{0.079 \times 0.05}\ \text{Sec}$$

$[t_{1/2}]_2$ = **253 Sec Answer**

So, in 253 seconds, the half of HI i.e. $\frac{0.05}{2} = 0.025$ moles is decomposed.

Example (2):

In thermal decomposition of N_2O at 760 °C, the time required to decompose half of the reactant was 255 seconds at the initial pressure of 290mm Hg and 212 seconds at the initial pressure of 360mm Hg. Find the order of this reaction.

Ans. **Given Data:**

The initial pressure of N_2O are the initial concentration

a_1 = 290mmHg t_1 = 255 seconds

a_2 = 360mmHg t_2 = 212 seconds

Required:

Order of reaction = n = ?

Solution:

Formula:

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

Putting the values in the above equation

$$n = 1 + \frac{\log\left[\frac{255}{212}\right]}{\log\left[\frac{360}{290}\right]}$$

$$n = 1 + \frac{0.0802}{0.0940}$$

$n = 1 + 0.85 = 1.85 \approx 2$ **Answer**

1.85 is close to 2, hence the reaction is **second order**

Example (3):

A plot of Arrhenius equation for the thermal decomposition of N_2O_5 is shown in figure. Slope is found to be −5400K. Calculate the energy of activation of this reaction.

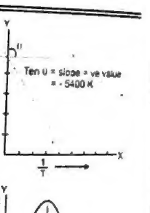
Ans. **Given Data:**

Slope of straight line = −5400K

Required:

Energy of activation = E_a = ?

Solution:



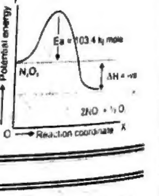
The reaction is $N_2O_5 \rightleftharpoons 2NO_2 + \frac{1}{2}O_2$

Equation used

$E_a = -\text{slope} \times 2.303R$

$R = 8.3143 JK^{-1} mole^{-1}$

Putting the values



$E_a = -(-54000K) \times 2.303 \times 8.3143 JK^{-1} mole^{-1}$

$E_a = +103401 J mole^{-1}$

$E_a = 103.401 kJ\ mole^{-1}$ **Answer**

Additional Questions

Q. Differentiate between Molecularity and Order of reaction.

Ans.

Molecularity	Order of reaction
1. It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change.	It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction.
2. It is always a whole number.	It may be a whole number, zero, fractional, positive or negative.
3. It is a theoretical concept.	It is experimentally determined.
4. It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaning less for overall complex reaction.	It is meant for the reaction and not for its individual steps.

Important Previous Board Questions

Q. Why the reactions having lower energies of activation have faster rates?

Q. The reactions happen due to collisions among the molecules but all the collisions are not fruitful. Justify it.

Q. What are the controlling factors on the activity of the enzyme?

For Answers study Scholar's CHEMISTRY (Objective) XI